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# Canadian Journal of Research

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OCTOBER, 1936

NUMBER 10

## THE HEAT CAPACITIES OF SILVER, NICKEL, ZINC, CADMIUM AND LEAD FROM $-80^{\circ}$ TO $120^{\circ}$ C.<sup>1</sup>

By H. L. BRONSON<sup>2</sup> AND A. J. C. WILSON<sup>3</sup>

### Abstract

The mean heat capacities over  $10^{\circ}$  intervals from  $-80^{\circ}$  to  $120^{\circ}$  C. have been determined for silver, nickel, zinc, cadmium and lead. The average deviation of the points from a smooth curve was in each case less than 0.1%, and it is believed that the absolute values are not in error by more than this amount.

The method used was the adiabatic electric heating of a kilogram or more of the metal in an all-copper jacket.

The following equations have been found to fit the curves with maximum deviations of about 0.1%:

Silver	$C_p = D(220/T) + 1.233 \times 10^{-5} T^{1.16},$
Nickel	$C_p = D(372/T) + 3.64 \times 10^{-6} T^{5/3},$
Zinc	$C_p = D(235/T) + 3.75 \times 10^{-6} T^{2/3},$
Cadmium	$C_p = D(160/T) + 9.63 \times 10^{-7} T^{5/3},$
Lead	$C_p = D(88/T) + 3.06 \times 10^{-6} T^{1.383},$

where  $D(\theta/T)$  is the Debye function and the units are joules per gram per  $^{\circ}$ C.

A discussion of the theoretical basis for the equations is given together with some calculations of heat capacities using data (coefficient of expansion, compressibility, etc.) involving no measurements of heat.

As a matter of convenience and for purposes of comparison, tables of heat capacities at  $10^{\circ}$  intervals are given for each metal. Quadratic or linear equations which fit the experimental curves within 0.25% are also given.

### Introduction

This investigation is a continuation of previous work done on copper by Bronson, Chisholm and Dockerty (5, 8). The apparatus and experimental methods are quite similar to those employed previously. A specimen of the metal whose heat capacity it is desired to determine is fitted with a heating coil and supported in a heavy copper jacket (Fig. 1). Satisfactory adiabatic conditions are maintained by heating coils on the outer surface of the jacket. A sensitive thermocouple between specimen and jacket serves to indicate any change in temperature. The temperature of the specimen is found by measuring that of the jacket with a platinum thermometer when the thermocouple indicates that there is no temperature difference between them.

The following is a brief outline of the experimental procedure. The jacket and specimen are brought to the same temperature, and the temperature is measured as described above. Both are then heated about  $10^{\circ}$  C., the

<sup>1</sup> Manuscript received September 4, 1936.

Contribution from the Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada.

<sup>2</sup> Professor of Physics, Dalhousie University.

<sup>3</sup> Holder of a bursary under the National Research Council of Canada.

electric energy supplied to the specimen being measured carefully. After the heating the temperature is again determined. Adiabatic conditions are carefully maintained throughout the above procedure. The heat capacity of the specimen is then found by dividing the energy supplied by the product of the "equivalent mass" of the specimen and the change in temperature.

The masses, electric energies and temperature changes were measured with a precision of about 0.01%, but the accuracy of the results is limited by a number of systematic errors discussed in a subsequent section.

If the number of thermojunctions between specimen and jacket is to be kept within reasonable limits, it is necessary to adjust the heating coils on the jacket and the thermal insulation surrounding it until the temperature variations over the inside surface are small. The jacket used by Dockerty (8) was unnecessarily troublesome because it was not of pure copper, and because the ground joint between its cover and body involved a certain lack of symmetry. A new jacket of pure copper was therefore made of two similar pieces with the ground joint at the centre of its side (Fig. 1).

#### Jacket Apparatus

To prevent possible heat losses along the lead wires passing through the jacket, a narrow groove was cut in one of the ground surfaces so that the leads passed half-way around the jacket before reaching a region of lower temperature.

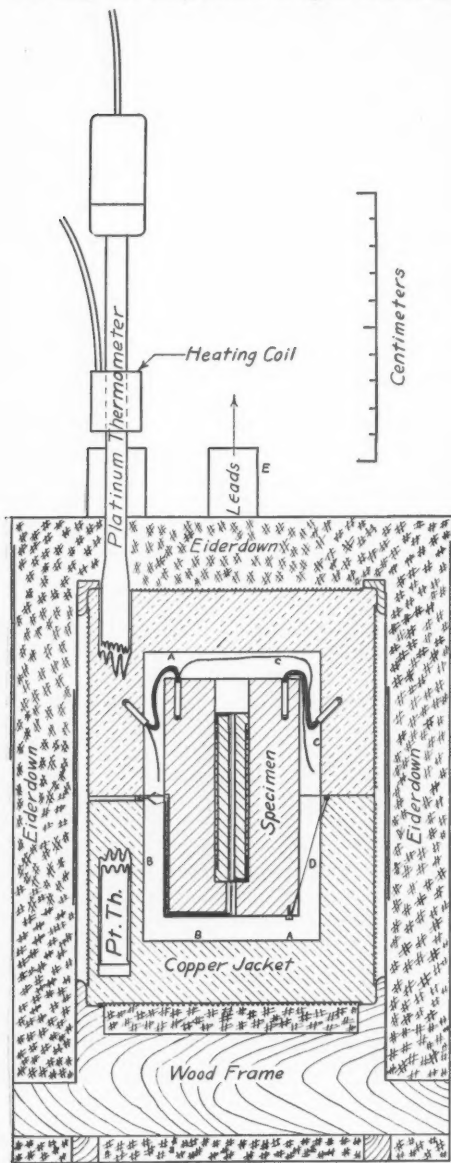


FIG. 1. The calorimeter.

The heating coils were wound on the outside of the jacket in spiral grooves. The resistances of the side and end windings were approximately in the ratio of the volumes of copper to be heated by each. Eiderdown was used for thermal insulation.

The insulation surrounding the jacket and the heating currents in the coils were adjusted as described by Dockerty until temporary pairs of thermojunctions indicated no temperature differences greater than  $0.01^{\circ}\text{C}$ . over the inner surface, either when the temperature was rising  $\frac{1}{3}^{\circ}$  per minute (the usual rate during an experiment) or was kept constant at  $100^{\circ}\text{C}$ . The approximate positions of the temporary pairs of thermojunctions are indicated in Fig. 1 by the letters *A-A*, *B-B*, *C-C*. A small heating coil was used on the stem of the thermometer as described by Dockerty to prevent disturbances due to conduction of heat along it.

In spite of these adjustments the thermocouple *A-A* indicated a temporary temperature difference of  $0.06^{\circ}\text{C}$ . when the heating current was first turned on or off. This difference was of short duration and was in opposite directions at the beginning and end of an experiment, so that the resultant heat transfer caused by this disturbance should be quite negligible.

#### *Thermocouples*

Temperature equality between specimen and jacket during an experiment was indicated by four two-junction copper-constantan thermocouples connected in series. Two of these are shown in Fig. 1; the other two are symmetrically situated at the lower half of the specimen and jacket. This distribution of thermocouples should eliminate most of the heat transfer due to any non-uniformity of temperature in either specimen or jacket.

#### *Platinum Thermometer*

A Leeds and Northrup calorimetric platinum thermometer connected to a Mueller bridge was used to measure the temperature change. The bridge originally had no thermostatic control, and the room in which it was used proved to have temperature variations sufficient to cause quite appreciable errors in the temperature measurements. To eliminate this trouble the housing of the bridge was changed to a copper lined box with a distributed heating coil, a de Khotinsky thermoregulator and a celluloid cover. This simple air thermostat controlled the temperature satisfactorily.

#### *Specimens*

The International Nickel Company of Canada presented the specimens of silver and nickel, and the Consolidated Mining and Smelting Company of Canada the specimens of zinc, cadmium and lead. Both companies were exceedingly kind and did everything possible to facilitate the investigation, supplying specially purified specimens carefully finished to the size and shape desired. The chemical analyses given below were also supplied by the companies.

Each specimen was prepared for the calorimeter\* as follows: A 0.5 in. hole was bored 3 in. deep along the axis of a cylinder of the metal 3.5 by 2 in. The heating coil was wound in a spiral groove cut in another cylinder of the same metal 2.5 by 0.5 in. which fitted neatly in the large cylinder. Three fine wires, one of which is shown at *D*, Fig. 1, supported the specimen in the jacket.

### Measurements

The following general outline of procedure indicates the care taken to discover and eliminate any possible source of systematic error. One or more series of measurements were made between 20° and 120° C., on each metal with the calorimeter protected from drafts merely by a wooden box. Then another series was taken with the calorimeter supported on wooden blocks inside a carefully insulated container. The jacket and specimen were then cooled below -80° C. with liquid air, and another series of measurements taken from -80° to 30° C., with the space surrounding the calorimeter filled with solid carbon dioxide. The calorimeter was then allowed to cool overnight without the use of liquid air, and another series taken from about -35° to 40° C. with comparatively little carbon dioxide around the calorimeter. Finally after the carbon dioxide had completely evaporated, the series between 20° and 120° C. was repeated to make sure that no changes had taken place in the apparatus. Each series occupied from 8 to 11 hr.

As will be seen later the above series of measurements were all in close agreement at room temperature. Nevertheless it seemed desirable to make a still further check using quite different apparatus. Measurements were therefore made on each metal between 10° and 50° C. with the water bath and jacket of Bronson, Chisholm and Dockerty (5). The measurements on lead were carried up to 95° C. by means of their oil bath.

The measured values of the heat capacities were plotted against temperature to a large scale and smooth curves were drawn through all the points. The number of observed points and the mean deviation of the individual points from each curve are shown in Table I.

TABLE I

Metal	No. of observed points	Mean deviation, %
Silver	58	0.03
Nickel	58	0.07
Zinc	75	0.05
Cadmium	97	0.05
Lead	75	0.10

Tables IV to VIII give the values of the heat capacities at 10° intervals as read from the curves. These values are believed to have an absolute accuracy of 0.1%, and relative accuracies somewhat greater than this except in the case of lead, in which case the error may reach 0.2% because of its low heat capacity and somewhat larger radiation loss due to its darker color.

\* Though the word is not exactly appropriate it is convenient to use "calorimeter" to refer to the whole assembly shown in Fig. 1.

## Sources of Error

The following is a brief discussion of the various sources of systematic errors with some indication of their magnitude.

The potentiometer, volt box, resistance and platinum thermometer bridge were calibrated several times during the course of the work. The fundamental interval of the platinum thermometer was determined frequently. It was considered safe to use the values of  $\delta$  and  $\gamma$  supplied by Leeds and Northrup. The total error due to the above is believed not to be over 0.05%.

The equivalent mass of each specimen was obtained as in the example shown. It is assumed that the thermocouples and hanging wires are heated half by the specimen and half by the jacket, and that the air is heated by the jacket and specimen in the ratio of their surfaces.

	Mass, gm.	Specific heat, cal. per °C. per gm.	Silver equivalent, gm.	Mass heated by specimen, gm.
<i>Heating coil</i>				
Copper wire	0.10	0.091	0.16	
Constantan wire	0.10	0.1	0.18	
Silk	0.05	0.4	0.36	
Cotton	0.03	0.37	0.20	
Shellac	0.01	0.4	0.07	
			0.97	0.97
<i>Brass screws</i>	0.43	0.092	0.71	0.71
<i>Thermocouples</i>				
Brass ends	2.22	0.092	3.65	
Copper wire	0.12	0.091	0.19	
Constantan wire	0.15	0.1	0.27	
Cotton	0.13	0.37	0.86	
Shellac	0.04	0.4	0.29	
Cement	0.08	0.2	0.29	
			5.55	2.78
<i>Hanging wires</i>	0.10	0.1	0.18	0.09
<i>Air</i>				0.38
				4.93
<i>Silver</i>	1839.4	0.056	1839.4	
	Equivalent mass of silver			1884.3
	Similarly,			1560.4
	nickel			1257.6
	zinc			1523.9
	cadmium			2018.5
	lead			

A rough estimate indicates that the error in these masses should be not more than 0.03% for the first four metals, or 0.05% for lead.

At times a downward drift in temperature was found even when the temperature of the jacket was kept equal to that of the specimen. The drift was especially troublesome with nickel and zinc but was occasionally noticed

with the others. It was suspected that the drift was due to the evaporation of a thin film of moisture from the surface of the specimen. It was found that baking the specimen for a few hours at  $110^{\circ}\text{C}$ . stopped the drift for several days. When the drift was greater than  $0.01^{\circ}$  per hour the measurements were rejected. In a few cases when the drift was less than this, corrections up to about  $0.05\%$  were applied.

The platinum thermometer does not measure the temperature of the jacket but the temperature of a particular part of the jacket that may not be at the mean temperature of the junctions of the thermocouples. Temperature variations in the jacket are a function of its temperature, being zero when the jacket is at the temperature of its surroundings. The original adjustment of the heating and insulation were such that it is not believed that this error can be more than  $0.002^{\circ}$  in a  $10^{\circ}$  interval, *i.e.*, an error of  $0.02\%$ .

The most difficult error to estimate would seem to be the heat transfer between specimen and jacket. Experiments made to discover the effect of lack of balance of the thermocouples showed that a constant difference in temperature between specimen and jacket of  $0.01^{\circ}$  would cause an error ranging from  $0.04\%$  (cadmium) to  $0.08\%$  (lead). Except for a few seconds at the beginning and end of a measurement, no difficulty was found in keeping the difference in temperature indicated by the thermocouples well within  $0.01^{\circ}$ . Since this difference varies at random from  $+$  to  $-$  the resultant accidental error should be very small. However, there might be a systematic error due to heat transfers even when the thermocouples indicated equal temperatures. The care taken in adjusting the heating and thermal insulation and the positions of the junctions of the thermocouples make it seem very unlikely that this error could be as large as that due to a  $0.01^{\circ}$  temperature difference.

The best evidence that lack of uniformity in the jacket temperature introduces no serious errors is a comparison of the results obtained at room temperature under three widely differing conditions, as shown in Table II. A further check on the reliability of the results given in this paper is furnished

TABLE II  
SPECIFIC HEAT

Metal	Temp., $^{\circ}\text{C}$ .	Cu jacket in $\text{CO}_2$ at $-80^{\circ}\text{C}$ .	Cu jacket in air at $20^{\circ}\text{C}$ .	Thin brass jacket in water bath
Ag	20	0.2338	0.2337	0.2336
Ni	20	0.4397	0.4395	0.4395
Zn	20	0.3885	0.3881	0.3881
Pb	20	0.1276 <sub>s</sub>	0.1276	0.1277 <sub>s</sub>
Cd	25	0.2316	0.2313	0.2313

by some unpublished measurements ( $10^{\circ}$  to  $120^{\circ}\text{C}$ .) obtained by one of the writers and E. W. Hewson on the silver and nickel specimens. The method was similar but the apparatus almost entirely different. Although the accuracy was somewhat less than that of the present work the results agree to within  $0.1\%$ .

### Theory

The heat capacity of a conductor is made up chiefly of three parts—the heat capacity of the atomic oscillations  $C_v$ , the work done against cohesive forces and the heat capacity of the conduction electrons  $c_e$ . In the tem-



perature range covered by the present work these parts are approximately 90, 10 and 1% respectively.

The usual expression for  $C_v$  is that derived by Debye (2),

$$C_v = 3R \left\{ \frac{12}{\left(\frac{\theta}{T}\right)^3} \int_0^{\frac{\theta}{T}} \frac{y^3 dy}{e^y - 1} - \frac{3\left(\frac{\theta}{T}\right)}{e^{\frac{\theta}{T}} - 1} \right\} \equiv D(\theta/T)$$

where  $\theta$  is the so-called "characteristic temperature",  $R$  the gas constant and  $T$  the absolute temperature. According to the Debye theory,  $\theta$  is related to the velocity of sound in the solid and can be calculated from elastic constants. It can also be found from measurements of the coefficient of expansion, or, empirically, from measurements of heat capacity at low temperatures where the work against cohesive forces is negligible.

The work done against cohesive forces is given by  $\frac{\alpha^2 T}{\rho\beta}$ , where  $\alpha$  is the temperature coefficient of volume expansion,  $\rho$  the density and  $\beta$  the volume compressibility.

On the assumption that the conduction electrons are "free", *i.e.*, act as a perfect gas obeying Fermi-Dirac statistics, their heat capacity (22) may be expressed as  $c_v = \frac{1}{2}\pi^2 \frac{kR}{\epsilon_0} T$  for all ordinary temperatures.  $k$  is the gas constant per molecule,  $\epsilon_0$  the maximum energy in the Fermi distribution at  $T = 0$ .

It would therefore be expected that the heat capacity of an isotropic metal would be given by

$$C_p = D(\theta/T) + \frac{\alpha^2 T}{\rho\beta} + \frac{1}{2}\pi^2 \frac{kR}{\epsilon_0} T \quad (1)$$

and of an anisotropic metal by

$$C_p = \frac{1}{3} \left\{ D\left(\frac{\theta_1}{T}\right) + D\left(\frac{\theta_2}{T}\right) + D\left(\frac{\theta_3}{T}\right) \right\} + \frac{(\alpha_1 + \alpha_2 + \alpha_3)^2 T}{\rho(\beta_1 + \beta_2 + \beta_3)} + \frac{1}{2}\pi^2 \frac{kR}{\epsilon_0} T \quad (2)$$

where  $\theta_1, \theta_2, \theta_3$  are the characteristic temperatures corresponding to the three axes of the crystal;  $\alpha_1, \alpha_2, \alpha_3$ , the linear expansion coefficients; and  $\beta_1, \beta_2, \beta_3$ , the linear compressibilities.

Unfortunately the use of Equation (1) or (2) involves several difficulties.

- (a) The characteristic temperature  $\theta$  varies with the temperature. Blackman (3) has developed an approximate lattice theory which gives a qualitative explanation of its variation at low temperatures. Also, since  $\theta$  is an increasing function of the density it should decrease as the temperature rises and the metal expands. Further, according to Damköhler (7), at sufficiently high temperatures  $\theta$  must increase, since the restoring force on the atoms increases faster than the displacement when the amplitude of oscillation becomes large.
- (b) There is much disagreement among the values of  $\alpha$  obtained by different observers. For most metals the only reliable determinations of  $\beta$  seem to be those of Bridgman (4) at 30° and 75° C.

(c) The expression for  $c_v$  can be expected to hold only for such metals as silver, copper and the alkali metals in which the conduction electrons act very nearly as though free.

In spite of these difficulties it is of some interest to calculate  $C_p$  from Equation (1) or (2) at 30° and 75° C. and compare it with the measured values. (The values of  $\theta$  were calculated from elastic constants by Schrödinger or from measurements of coefficients of expansion by Grüneisen and Goens (10).) The agreement (Table III) is rather striking when it is realized that no calorimetric data whatever have been used in the calculations.

TABLE III  
COMPARISON OF THE OBSERVED HEAT CAPACITIES WITH THOSE CALCULATED FROM ELASTIC CONSTANTS, ETC.

Temp. °C.	Metal	$\theta$	$D(\theta/T)$	$\frac{\alpha^2 T}{\rho\beta}$	$c_v$	$C_p$ calc.	$C_p$ exp.	Diff. %
20	Cd	160-214 214	0.2169	0.0131	0.0019	0.2319	0.2319	—
30	Ag	220	0.2252	0.0091	0.0018	0.2361	0.2345	0.7
	Zn	200 320 320	0.3652	0.0202	0.0028	0.3882	0.3900	-0.5
	Pb	75	0.1200	0.0086	0.0014	0.1300	0.1281	1.5
	Cu	341	0.3685	0.0115	0.0024	0.3824	0.3850	-0.7
75	Ag		0.2266	0.0109	0.0021	0.2396	0.2377	0.8
	Zn		0.3690	0.0236	0.0032	0.3958	0.3972	-0.4
	Pb		0.1201	0.0108	0.0016	0.1325	0.1301	1.8
	Cu		0.3745	0.0142	0.0028	0.3915	0.3926	-0.3
								Av. 0.7

NOTE.—Sources of data,

$\theta$ . Ag, Pb, Cu: (20).  
Zn, Cd: (10, 12).

$\alpha$ . Ag, Pb, Cu: (13).

Zn: (14, 18, 1). Cd: (10).

$\beta$ . (4).  $\rho$ . (11).

$C_p$  of Cu (8).

Nickel has been omitted from the comparison because part of its heat capacity is due to its ferromagnetism. On the Weiss theory of magnetism, the "énergie de désaimantation" may be calculated from  $C_m = -\frac{1}{2}n \frac{dI^2}{dT}$ , where  $I$  is the intensity of spontaneous magnetisation and  $n$  a coefficient which can be obtained from magnetic measurements. Besides this however there is a "terme inconnu"\* for which there seems to be no quantitative theory (16).

### Empirical Equations

Aside from uncertainties in the theory and the lack of numerical data for the constants, Equations (1) and (2) are too complicated to be useful in representing the numerical results. Dockerty (8) found it possible to replace  $\left(\frac{\alpha^2}{\rho\beta} + \frac{1}{2}\pi^2 \frac{kR}{\epsilon_0}\right)^\dagger T$  for copper by a term  $AT$ , but this does not increase suffi-

\* Stoner, E. C. (23) and Mott, N. F. (17) have shown that this is probably the heat capacity of the electrons, which have a very small value of  $\epsilon_0$  in nickel.

† If  $\frac{\alpha^2}{\rho\beta}$  were constant this expression would be proportional to  $T$ . However,  $\alpha$  increases fairly rapidly with  $T$ . Theoretically  $\alpha = \rho\beta\gamma C_v$ , where  $\gamma = d \log \theta / d \log \rho$ . Grüneisen's empirical law states that  $\alpha$  is proportional to  $C_p$ , but in many cases it seems to increase faster than  $C_p$  or  $C_v$ . Because of this and the clumsiness of the form no attempt was made to replace  $\frac{\alpha^2}{\rho\beta}$  by the usual expressions  $GC_p^2 T$  or  $G'C_p^2 T$ .



ciently rapidly with  $T$  to give a good representation of the heat capacity of silver, nickel, zinc, cadmium or lead. Since the expression  $AT$  with a single empirical constant was found unsuitable, the expressions  $AT + BT^2$  and  $AT^n$  containing two empirical constants were tried. Either form can be made to fit the experimental results within about 0.1% between  $-80^\circ$  and  $120^\circ$  C., but on the whole  $AT^n$  seemed slightly more satisfactory.

The numerical values of  $A$ ,  $\theta$  and  $n$  were determined as follows: no attempt was made to use the values of  $\theta$  employed in Table I derived from elastic constants. Instead,  $A$ ,  $n$  and  $\theta$  were determined empirically as follows: what appeared to be the best value of  $\theta$  found by experimenters at low temperatures was assumed, and  $D(\theta/T)$  calculated at  $10^\circ$  intervals for each metal. The values of  $D(\theta/T)$  were subtracted from the experimental values of  $C_p$  read from the curves and the differences plotted against  $T$  on logarithmic paper. If the resulting curve was a straight line,  $A$  and  $n$  were determined from it. If it were not it could be made approximately straight by slightly changing the value of  $\theta^*$ . The following equations, thus found, fit the curves and the maximum deviations are noted:

Silver	$C_p = D(220/T) + 1.23_3 \times 10^{-5} T^{1.16}$	Maximum deviation 0.04%	(3)
Nickel	$C_p = D(372/T) + 3.64 \times 10^{-6} T^{5/3}$	Maximum deviation 0.1%	(4)
Zinc	$C_p = D(235/T) + 3.75 \times 10^{-6} T^{3/2}$	Maximum deviation 0.07%	(5)
Cadmium	$C_p = D(160/T) + 9.63 \times 10^{-7} T^{3/3}$	Maximum deviation 0.1%	(6)
Lead	$C_p = D(88/T) + 3.06 \times 10^{-6} T^{1.33_3}$	Maximum deviation 0.15%	(7)

In Tables IV to VIII heat capacities calculated at  $10^\circ$  intervals from these equations are compared with values obtained from the curve drawn through the experimental values. In a paper to be published (6) it is shown that the above equation for silver may be extrapolated quite satisfactorily up to  $500^\circ$  C. and for nickel up to  $250^\circ$  C.

For convenience in calculation when a smaller degree of accuracy is required quadratic or linear equations together with their maximum deviations from the experimental curves are also given:

Silver	$C_p = 0.2321 + 9.8 \times 10^{-5} t - 2.6 \times 10^{-7} t^2$	Maximum deviation 0.15%	(8)
Nickel	$C_p = 0.4298 + 5.42 \times 10^{-4} t - 9.3 \times 10^{-7} t^2$	Maximum deviation 0.25%	(9)
Zinc	$C_p = 0.3848 + 2.08 \times 10^{-4} t - 4.6 \times 10^{-7} t^2$	Maximum deviation 0.2%	(10)
Cadmium	$C_p = 0.2288 + 9.8 \times 10^{-5} t$	Maximum deviation 0.2%	(11)
Lead	$C_p = 0.1269 + 4.2 \times 10^{-5} t$	Maximum deviation 0.15%	(12)

The shapes of the quadratic equations are obviously wrong, and the differences between their slopes and the slopes of the experimental curves at the ends of the range are so great that these equations are unsuitable for extrapolation.

\* Beattie (2) has tabulated  $\frac{1}{3R} D(\theta/T)$  and  $\frac{1}{3RT} U(\theta/T) = \frac{1}{3RT} \int_0^T D(\theta/T) dT$  to six places.

Since his tables are not arranged for easy interpolation and since  $\frac{1}{3R} D(\theta/T)$  must be multiplied

by the appropriate value of  $3R$  before use, a table of  $\log \frac{1}{3R} D(\theta/T)$  was formed from the part of his table covering the range required in the present work (Table IX).  $3R$  was taken as 24.943 joules per mole  $^\circ\text{C}$ .

A plot of  $T^n$  against  $T$  on logarithmic paper will be found useful if a large number of values of  $AT^n$  have to be calculated.

### Discussion of Particular Metals

#### Silver

Analysis: Ag 99.98+, Cu 0.0095, Fe 0.0018%.

The value for  $\theta$  given by Schrödinger (20) is 215. Keesom and Clark (15) found the value for  $\theta$  to be, 210 at 20° K, 220 at 8° K, 236 at 5° K and 224 at 2.5° K. The value 220 gave the best straight line in the plot of  $C_p - D(\theta/T)$ , so it was chosen for use in Equation (3).

Griffiths and Griffiths (9) have measured the heat capacity of silver between 0° and 97.5° C. by a method involving the differential electric heating of two similar masses of metal. Their experimental values are about 0.25% higher than the writers' value at 0°, and 0.5% higher at 100° C.

#### Nickel

Analysis: Ni 99.69, Cu 0.03, Fe 0.13, Si 0.10, C 0.03%, Mg trace.

Some of the modern values of  $\theta$  are here indicated. Rodebush and Michalek (19), 372; Simon and Ruhemann (21), 368; Lapp (16), 380. The value 372 was chosen as a weighted mean. Since the magnetic terms form a large part of the heat capacity of nickel there was no reason to expect that  $C_p - D(\theta/T)$  could be represented by  $AT^n$  but Equation (4) gives good agreement with experiment.

#### Zinc

Analysis: Zn 99.98, Pb 0.009, Cd 0.004, Cu 0.001, Fe 0.0014%.

The value 235 is given by Schrödinger for  $\theta$ , and was used in Equation (5).

The experimental values of Griffiths and Griffiths are lower than the writers' by about 0.25% at 0°, and 0.5% at 100° C.

#### Cadmium

Analysis: Cd 99.97, Pb 0.010, Zn 0.022, Cu 0.002, Fe 0.0001%.

The value 168 is given by Schrödinger for  $\theta$ . This is too large to give a satisfactory straight line in the plot of  $C_p - D(\theta/T)$ , so the value 160 was used in Equation (6).

The experimental results of Griffiths and Griffiths are higher than the writers' results by about 0.25%.

#### Lead

Analysis: Pb 99.997, Ag 0.0006, Cu 0.0009, Sb 0.0007, Bi 0.0002%.

The value of 88 given by Schrödinger for  $\theta$  was used in Equation (7).

The experimental values of Griffiths and Griffiths are lower than the writers' value by about 0.5% at 0°, and 0.25% at 100° C.

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TABLE IV  
THE HEAT CAPACITY OF SILVER IN JOULES PER GRAM PER °C.

Temp. °C.	$C_p$	$C_p$ Eq. 3.	Diff.	Temp. °C.	$C_p$	$C_p$ Eq. 3	Diff.
-80	0.2224	0.2224	0	30	0.2345 <sub>s</sub>	0.2346	0 <sub>s</sub>
-70	0.2241	0.2241	0	40	0.2353	0.2353	0
-60	0.2255 <sub>s</sub>	0.2255 <sub>s</sub>	0	50	0.2360	0.2360	0
-50	0.2269	0.2268 <sub>s</sub>	-0 <sub>s</sub>	60	0.2367	0.2366 <sub>s</sub>	-0 <sub>s</sub>
-40	0.2281	0.2281	0	70	0.2373 <sub>s</sub>	0.2373	-0 <sub>s</sub>
-30	0.2292	0.2292	0	80	0.2380	0.2379	-1
-20	0.2303	0.2303	0	90	0.2386	0.2385	-1
-10	0.2313	0.2312 <sub>s</sub>	-0 <sub>s</sub>	100	0.2392	0.2391 <sub>s</sub>	-0 <sub>s</sub>
0	0.2321 <sub>s</sub>	0.2321 <sub>s</sub>	0	110	0.2397	0.2397	0
10	0.2330	0.2330	0	120	0.2402 <sub>s</sub>	0.2403	0 <sub>s</sub>
20	0.2338	0.2338	0				

TABLE V  
THE HEAT CAPACITY OF NICKEL IN JOULES PER GRAM PER °C.

Temp. °C.	$C_p$	$C_p$ Eq. 4.	Diff.	Temp. °C.	$C_p$	$C_p$ Eq. 4	Diff.
-70	0.3872	0.3869	-3	30	0.4443	0.4444	1
-60	0.3945	0.3941	-4	40	0.4488	0.4490	2
-50	0.4010	0.4011	1	50	0.4533	0.4533	0
-40	0.4073	0.4075	2	60	0.4576	0.4579	3
-30	0.4133	0.4135	2	70	0.4619	0.4622	3
-20	0.4191	0.4192	1	80	0.4663	0.4664	1
-10	0.4247	0.4246	-1	90	0.4705	0.4709	4
0	0.4299	0.4300	1	100	0.4747	0.4751	4
10	0.4348	0.4348	0	110	0.4790	0.4791	1
20	0.4398	0.4396	-2				

TABLE VI

THE HEAT CAPACITY OF ZINC IN JOULES PER GRAM PER °C.

Temp. °C.	$C_p$	$C_p$ Eq. 5.	Diff.	Temp. °C.	$C_p$	$C_p$ Eq. 5	Diff.
-80	0.3646 <sub>5</sub>	0.3648	1 <sub>5</sub>	30	0.3900	0.3901	1
-70	0.3680	0.3680	0	40	0.3917 <sub>5</sub>	0.3917	-0 <sub>5</sub>
-60	0.3710	0.3709	-1	50	0.3933	0.3933	0
-50	0.3738	0.3736	-2	60	0.3948	0.3949 <sub>5</sub>	1 <sub>5</sub>
-40	0.3763 <sub>5</sub>	0.3761	-2 <sub>5</sub>	70	0.3964	0.3965	1
-30	0.3786	0.3784 <sub>5</sub>	-1 <sub>5</sub>	80	0.3979	0.3980	1
-20	0.3807 <sub>5</sub>	0.3806 <sub>5</sub>	-1	90	0.3995	0.3994 <sub>5</sub>	-0 <sub>5</sub>
-10	0.3828	0.3827	-1	100	0.4010	0.4010	0
0	0.3848	0.3847	-1	110	0.4025	0.4024	-1
10	0.3866	0.3865	-1	120	0.4040	0.4040	0
20	0.3883	0.3883	0				

TABLE VII

THE HEAT CAPACITY OF CADMIUM IN JOULES PER GRAM PER °C.

Temp. °C.	$C_p$	$C_p$ Eq. 6.	Diff.	Temp. °C.	$C_p$	$C_p$ Eq. 6	Diff.
-80	0.2206	0.2206 <sub>5</sub>	0 <sub>5</sub>	20	0.2310	0.2310 <sub>5</sub>	0 <sub>5</sub>
-70	0.2219	0.2219	0	30	0.2319	0.2320	1
-60	0.2231	0.2232	1	40	0.2328 <sub>5</sub>	0.2329	0 <sub>5</sub>
-50	0.2242	0.2241 <sub>5</sub>	-0 <sub>5</sub>	50	0.2338	0.2338	0
-40	0.2252	0.2252 <sub>5</sub>	0 <sub>5</sub>	60	0.2347 <sub>5</sub>	0.2347 <sub>5</sub>	0
-30	0.2262	0.2262 <sub>5</sub>	0 <sub>5</sub>	70	0.2357	0.2357	0
-20	0.2272 <sub>5</sub>	0.2272 <sub>5</sub>	0	80	0.2367	0.2366	-1
-10	0.2282	0.2282	0	90	0.2377	0.2375	-2
0	0.2291 <sub>5</sub>	0.2291 <sub>5</sub>	0	100	0.2386 <sub>5</sub>	0.2385	-1 <sub>5</sub>
10	0.2300 <sub>5</sub>	0.2301 <sub>5</sub>	1	110	0.2396 <sub>5</sub>	0.2395	-1 <sub>5</sub>

TABLE VIII

THE HEAT CAPACITY OF LEAD IN JOULES PER GRAM PER °C.

Temp. °C.	$C_p$	$C_p$ Eq. 7	Diff.	Temp. °C.	$C_p$	$C_p$ Eq. 7	Diff.
-70	0.1241 <sub>5</sub>	0.1240 <sub>5</sub>	-1	30	0.1281	0.1282	1
-60	0.1245	0.1244 <sub>5</sub>	-0 <sub>5</sub>	40	0.1285	0.1286	1
-50	0.1249	0.1248 <sub>5</sub>	-0 <sub>5</sub>	50	0.1290	0.1289	-1
-40	0.1252 <sub>5</sub>	0.1253	0 <sub>5</sub>	60	0.1294	0.1293 <sub>5</sub>	-0 <sub>5</sub>
-30	0.1256 <sub>5</sub>	0.1257	0 <sub>5</sub>	70	0.1299	0.1298 <sub>5</sub>	-0 <sub>5</sub>
-20	0.1260	0.1261	1	80	0.1303	0.1302	-1
-10	0.1264	0.1265	1	90	0.1307 <sub>5</sub>	0.1306	-1 <sub>5</sub>
0	0.1268	0.1269 <sub>5</sub>	1 <sub>5</sub>	100	0.1312	0.1310 <sub>5</sub>	-1 <sub>5</sub>
10	0.1272 <sub>5</sub>	0.1273	0 <sub>5</sub>	110	0.1316	0.1314 <sub>5</sub>	-1 <sub>5</sub>
20	0.1277	0.1277	0	120	0.1321	0.1319	-2

$\theta/T$	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09	1	2	3	4	5	1	2	3	4	5			
.0		9	9999	9998	9997	9995	9992	9989	9986	9982	2	0	0	1	1	1	4	0	1	1	2	2	
			1	1	2	3	3	3	4	4													
.1	9	9978	9974	9969	9963	9957	9951	9944	9937	9930	9922	6	1	1	2	2	3	8	1	2	2	3	4
		4	5	6	6	6	7	7	7	8	9												
.2	9	9913	9904	9895	9885	9875	9864	9853	9842	9830	9818	10	1	2	3	4	5	12	1	2	4	5	6
		9	9	10	10	11	11	11	12	12	13												
.3	9	9805	9792	9778	9764	9749	9734	9719	9703	9687	9670	14	1	3	4	6	7	16	2	3	5	6	8
		13	14	14	15	15	15	16	16	17	17												
.4	9	9653	9636	9618	9599	9580	9561	9542	9522	9501	9480	18	2	4	5	7	9	20	2	4	6	8	10
		17	18	19	19	19	19	20	21	21	21												
.5	9	9459	9437	9415	9392	9369	9345	9321	9297	9272	9247	22	2	4	7	9	11	24	2	5	7	10	12
		22	22	23	23	24	24	24	25	25	26												
.6	9	9221	9195	9169	9142	9114	9087	9058	9030	9001	8971	26	3	5	7	10	13	28	3	6	8	11	14
		26	26	27	28	27	29	28	29	30	29												
.7	9	8942	8911	8880	8849	8818	8786	8753	8721	8687	8654	30	3	6	9	12	15	32	3	6	10	13	16
		31	31	31	31	32	33	32	34	33	34												
.8	9	8620	8585	8550	8515	8479	8443	8407	8370	8332	8294	34	3	7	10	14	17	36	4	7	11	14	18
		35	35	35	36	36	36	37	38	38	38												
.9	9	8256	8218	8179	8139	8099	8059	8018	7977	7936	7894	38	4	8	11	15	19	40	4	8	12	16	20
		38	39	40	40	40	41	41	41	42	43												
1.0	9	7851	7809	7766	7722	7678	7634	7589	7544	7498	7452	42	4	8	13	17	21	44	4	9	13	18	22
		42	43	44	44	44	45	45	46	46	46												
1.1	9	7406	7359	7312	7265	7217	7168	7119	7070	7021	6971	46	5	9	14	18	23	48	5	10	14	19	24
		47	47	47	48	49	49	49	49	50	51												
1.2	9	6920	6870	6818	6767	6715	6663	6610	6557	6503	6449	50	5	10	15	20	25	52	5	10	16	21	26
		50	52	51	52	52																	

# THE HEAT CAPACITY OF SILVER AND NICKEL BETWEEN 100° AND 500° C.<sup>1</sup>

BY H. L. BRONSON<sup>2</sup>, E. W. HEWSON<sup>3</sup> AND A. J. C. WILSON<sup>4</sup>

## Abstract

The mean heat capacities of silver and nickel between 0° C. and various temperatures from 100° to 500° C. have been determined by the method of mixtures, an all-copper adiabatic calorimeter being used.

A brief discussion deals with the difficulty of obtaining accurate values of the true heat capacity,  $C_p$ , from mean heat capacity,  $\bar{C}_p$ , measurements.

The following table gives a brief summary of the results:

	100°	150°	200°	250°	300°	350°	400°	450°	500° C.
Silver									
$\bar{C}_p$	0.2364	0.2376	0.2389	0.2401	0.2415	0.2427	0.2440	0.2452	0.2465
$C_p$	0.2389	0.2413	0.2439	0.2463	0.2490	0.2514	0.2540	0.256	0.259
Nickel									
$\bar{C}_p$	0.4536	0.4636	0.4741	0.4856	0.4972	0.5117	0.5162	0.5177	0.5188
$C_p$	0.474	0.495	0.517	0.543	0.575	0.627	0.531	0.529	0.527

The uncertainty in  $\bar{C}_p$  of both silver and nickel is about 0.2%, in  $C_p$  of silver from about 0.2% at 100° C. to nearly 1% at 500° C., in  $C_p$  of nickel from about 0.5% at 100° C. to 2% at 350° C. and above.

## Apparatus and Measurements

The apparatus and methods used were the same as those of Bronson, Chisholm and Dockerty (2). The copper calorimeters were recalibrated before being used, and the platinum thermometer, bridge and thermocouples were calibrated at frequent intervals during the work. An improved electric furnace was constructed. The cylindrical specimens of silver and nickel were about 1.9 by 3.8 cm. in length. They were presented by the International Nickel Company of Canada, and their analyses were the same as that of the larger specimens used in previous work (3).

The heat given out by one gram of silver or nickel in cooling from various temperatures between 100° and 500° C. to about 25° C. was measured. To this was added the amount of heat which would have been given out in cooling from the final temperature to 0° C. The values of heat capacity found in a previous paper (3) were used in calculating the addition. Dividing the values of the total heat so found by  $t$ , the original temperature of the specimen, gives the mean value of the heat capacity over the range 0° to  $t$ ° C. The symbol  $\bar{C}_p$  will be used to represent this mean heat capacity,  $C_p$  to represent the heat capacity at  $t$ ° C. The experimental results are given in Tables I and II. Each value given is the mean of several determinations made at approximately the same temperature. The number of determinations averaged is given in the third column of the tables.

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Contribution from the Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada.

<sup>2</sup> Professor of Physics, Dalhousie University.

<sup>3</sup> At present, holder of a Beit Scientific Research Fellowship at Imperial College, London, England; at the time, demonstrator in physics, Dalhousie University.

<sup>4</sup> Holder of a bursary under the National Research Council of Canada.

TABLE I  
THE MEAN HEAT CAPACITY OF SILVER IN JOULES PER GRAM PER °C.

Temperature, °C.	$\bar{C}_p$		$\bar{C}_p + \text{corr.}$	$\bar{C}_p$ (Eq. 1)	Difference
106.4	0.2359	(5)	0.2364	0.2361	-3
147.9	0.2371	(5)	0.2376	0.2374	-2
203.7	0.2384	(4)	0.2389	0.2391	+2
238.0	0.2395	(2)	0.2400	0.2400	0
253.7	0.2399	(3)	0.2404	0.2403	-1
301.1	0.2409	(2)	0.2415	0.2414	-1
353.4	0.2420	(4)	0.2426	0.2428	+2
399.4	0.2433	(3)	0.2439	0.2440	+1
453.3	0.2447	(2)	0.2453	0.2452	-1
502.5	0.2458	(2)	0.2465	0.2463	-2

TABLE II  
THE MEAN HEAT CAPACITY OF NICKEL IN JOULES PER GRAM PER °C.

Temperature, °C.	$\bar{C}_p$		$\bar{C}_p + \text{corr.}$	$\bar{C}_p$ (Eq. 2)	Difference
105.9	0.4542	(5)	0.4548	0.4548	0
145.2 <sub>s</sub>	0.4622	(2)	0.4628	0.4626	-2
201.0	0.4739	(2)	0.4745	0.4745	0
254.3	0.4859	(3)	0.4865	0.4865	0
301.4	0.4967 <sub>s</sub>	(2)	0.4974	0.4966	-8
331.0	0.5050	(2)	0.5057	0.5039	-18
352.3	0.5118	(4)	0.5125	0.5073	-52
384.1	0.5150	(1)	0.5157	—	—
401.9	0.5157	(2)	0.5164	—	—
454.0	0.5172	(2)	0.5179	—	—
505.3 <sub>s</sub>	0.5181	(2)	0.5189	—	—

In the fifth column of the tables are given the values of  $\bar{C}_p$  calculated from the equations:

$$\text{Silver} \quad \bar{C}_p = \frac{3RT}{t} \left\{ \frac{1}{3RT} U(220/T) + 2.475 \times 10^{-5} T^{1.16} \right\} - 47.16/t \quad (1)$$

$$\text{Nickel} \quad \bar{C}_p = \frac{3RT}{t} \left\{ \frac{1}{3RT} U(372/T) + 3.22 \times 10^{-6} T^{5/3} \right\} - 71.63/t \quad (2)$$

where  $U(\theta/T)$  is the Debye energy function\*. These equations were derived from Equations (3) and (4) of a previous paper (3) by using the relation,

$$\bar{C}_p = \frac{1}{t} \int_{273.2}^{273.2+t} C_p dT \quad (3)$$

A comparison of Columns 2 and 5 of Tables I and II shows that the experimental values of  $\bar{C}_p$  for silver are about 0.2% lower than the calculated ones over the entire range of temperature, and that the experimental values of

\*Tables of this function have been given by Beattie (1).



$\bar{C}_p$  for nickel are slightly over 0.1% lower up to 250° C. Reference to the paper of Bronson, Chisholm and Dockerty (2) shows a similar difference of about 0.2% for copper.

In determining the experimental values of  $\bar{C}_p$  in Column 2 of the tables, no correction was made for heat lost by the specimen during its fall from the furnace to the calorimeter. The upper limit for the loss would seem to be black body radiation during the time of fall plus the heat required to bring all the air in the tube through which the specimen fell to the temperature of the specimen. An addition of half this maximum loss, Column 4 of the tables, was thought reasonable and brings the experimental values of  $\bar{C}_p$  for silver over the whole range and for nickel up to 250° C. into good agreement with the values of  $\bar{C}_p$  calculated from Equations 1 and 2. The corrected experimental points are plotted as circles in Figs. 1 and 2. The curves *DE* are the plots of Equations (1) and (2).

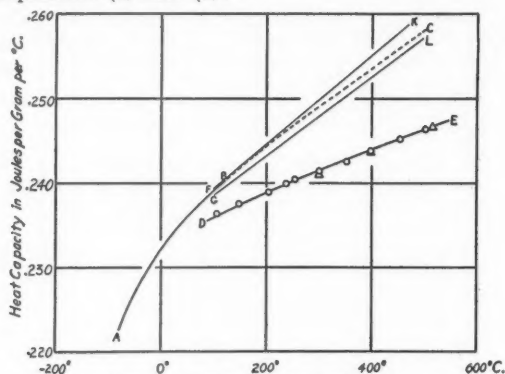


FIG. 1. The heat capacity of silver.

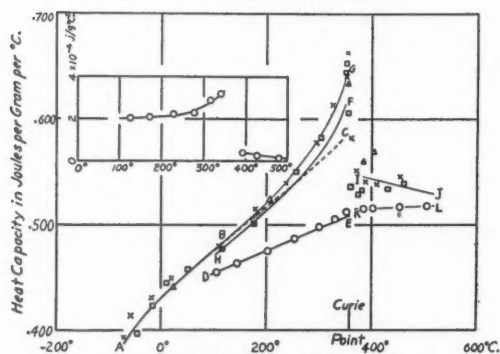


FIG. 2. The heat capacity of nickel.

It should be pointed out that the same correction added to the values of  $\bar{C}_p$  for copper found by Bronson, Chisholm and Dockerty (2) would have made the agreement with their electrical heating experiments better.



### Calculation of $C_p$ from $\bar{C}_p$

It has been frequently pointed out, but is not always realized, that values of  $C_p$  are considerably less accurate than the values of  $\bar{C}_p$  from which they are derived. The usual method of determining  $C_p$  from  $\bar{C}_p$  seems to be to fit an empirical equation to  $\bar{C}_p$  and use the relation:

$$C_p = \bar{C}_p + t \frac{d\bar{C}_p}{dt} \quad (4)$$

found by differentiating Equation (3). Fitting an equation to a total heat curve and differentiating it is mathematically identical with the above procedure. Equations devised to fit  $\bar{C}_p$  equally well may have quite different slopes, so that the values of  $C_p$  and even the form of the curve differ widely.

A striking example of this showed up in attempting to obtain a  $C_p$  curve for nickel above the Curie point from the writers' determinations of  $\bar{C}_p$ . The following three equations fit the experimental points well within the experimental error, the maximum deviation being 0.06%:

$$\bar{C}_p = 0.4847 + 1.23 \times 10^{-4} t - 1.1 \times 10^{-7} t^2 \quad (5)$$

$$\bar{C}_p = 0.5292 - 5.16/t \quad (6)$$

$$\bar{C}_p = 0.5072 + 2.3 \times 10^{-5} t \quad (7)$$

The corresponding  $C_p$  equations derived from these are:

$$C_p = 0.4847 + 2.46 \times 10^{-4} t - 3.3 \times 10^{-7} t^2 \quad (8)$$

$$C_p = 0.5292 \quad (9)$$

$$C_p = 0.5072 + 4.6 \times 10^{-5} t \quad (10)$$

Equation (8) represents  $C_p$  decreasing with  $t$ , (9)  $C_p$  constant and (10)  $C_p$  increasing. The equations and the experimental points are plotted in Fig. 3. It will be seen that there are differences of 1% between  $C_p$  equations, i.e., nearly twenty times the differences in the  $\bar{C}_p$  equations.

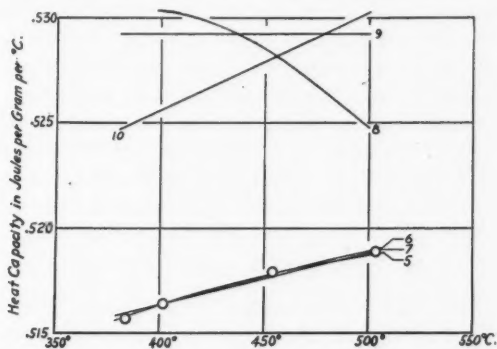


FIG. 3. Showing the large changes in the derived  $C_p$  curves (8, 9, 10) caused by small changes in the slope of the  $\bar{C}_p$  curves (5, 6, 7).

*C<sub>p</sub> of Silver*

The corrected experimental values of  $\bar{C}_p$  for silver are plotted as circles in Fig. 1. For comparison some of the values of  $\bar{C}_p$  for oxygen-free silver found by Jaeger, Rosenbohm and Veenstra (5) are plotted as triangles. The slope of our experimental  $\bar{C}_p$  curve shows no progressive changes between 100° and 500° C. but varies irregularly between  $2.2 \times 10^{-5}$  and  $2.8 \times 10^{-5}$  joules per gram per °C. Substituting these values in Equation (4) gives *FK* for the upper limit of  $C_p$  and *GL* for the lower limit. The curve *ABC* is the plot of the equation

$$C_p = D(220/T) + 1.233 \times 10^{-5} T^{1.16}$$

given in a previous paper (3) to represent  $C_p$  between -80° and 120° C. It falls between *FK* and *GL* everywhere, so it appears that this equation represents the heat capacity of silver satisfactorily between -80° and 500° C. The uncertainty is about 0.1% between -80° and 120° C., 0.5% at 300° C., 1% at 500° C.

TABLE III  
THE HEAT CAPACITIES OF SILVER AND NICKEL IN  
JOULES PER GRAM PER °C.

Temperature, °C.	<i>C<sub>p</sub></i> of silver	<i>C<sub>p</sub></i> of nickel
100	0.2389 ± .0005	0.474 ± .002
150	0.2413 ± .0007	0.495 ± .003
200	0.2439 ± .0008	0.517 ± .004
250	0.2463 ± .0009	0.543 ± .006
300	0.2490 ± .0011	0.575 ± .008
350	0.2514 ± .0013	0.627 ± .012
358 ± 2	—	Curie point
400	0.2540 ± .0014	0.531 ± .014
450	0.2564 ± .0016	0.529 ± .011
500	0.2588 ± .0017	0.527 ± .008

Table III, Column 2, gives the values of  $C_p$  for silver at 50° intervals derived from the values of  $\bar{C}_p$  in Column 4 of Table I by the use of Equation (4).

Although the values of  $\bar{C}_p$  found by Jaeger, Rosenbohm and Veenstra agree, to within about 0.2%, with those of the writers, their curve has a somewhat greater slope and so indicates a value for  $C_p$ , 0.5 to 1% higher than that given in Table III.

*C<sub>p</sub> of Nickel*

The corrected experimental values of  $\bar{C}_p$  for nickel are plotted as circles in Fig. 2. There is a discontinuity in the slope at  $358 \pm 2^\circ$  C. owing to the disappearance of one of the magnetic terms in the equation for the heat capacity. The slope of the  $\bar{C}_p$  curve is plotted in the inset. The error in determining the slope is such that the error in the values of  $C_p$  found by Equation (4) is about 2% near the Curie point, and 1% over the rest of the range. Table III, Column 3, gives the heat capacity of nickel at 50° intervals. The curves *BG* and *HF* give the limits of  $C_p$  below the Curie point, *IJ* and *KL* above the Curie point. The curve *ABC* is the plot of the equation:

$$C_p = D(372/T) + 3.64 \times 10^{-6} T^{5/3}$$

given in a previous paper (3) to represent  $C_p$  of nickel between -80° and 120° C. It will be seen that the equation is unsatisfactory above about 250° C. Some values of  $C_p$  found by Sucksmith and Potter (7) ( $\Delta$ ), Lapp (6) ( $\square$ ), and Grew (4) ( $\times$ ) by direct methods are plotted in Fig. 2 for com-

parison. Sucksmith and Potter do not find quite as large a change in  $C_p$  at the Curie point, but on the whole the agreement is about as good as can be expected, as each of the three different methods has an uncertainty of 1% or more.

### Acknowledgments

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## THE ALKALOIDS OF FUMARIACEOUS PLANTS

### XII. *CORYDALIS SCOULERI* Hk.<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup>

#### Abstract

Examination of this plant has disclosed the presence of ten alkaloids, five of which, namely, *protopine* (0.15%), *cryptopine* (0.004%), *α-allo-cryptopine* (0.001%), *bicuculline* (0.20%), and *scoulerine* (0.06%) are well known. A sixth proved to be identical with *capnoidine* (0.002%), an alkaloid hitherto found only in *Corydalis sempervirens*. Two of the remaining four, *corlumine* (0.12%) and *corluminidine* (0.02%), have been adequately characterized as phthalide isoquinolines and their respective constitutions determined in whole or in part. The last two appear to be new and are designated by Greek letters, namely, *-η* (0.002%), m.p. 180° C., probably isomeric with *adlumine* and *corlumine*, and *-θ* (0.002%), m.p. 183° C.,  $C_{16}H_{17}O_3N$ . The yield of pure crystallized total alkaloids was 0.56%.

*Corydalis scouleri* Hk. is endemic to the Pacific Coast of North America, extending only from southern British Columbia to Oregon or a little farther south. No *Corydalis* species of this limited habitat has hitherto been chemically examined. Its vigorous growth and general appearance are not common to members of this genus and it seemed therefore that a chemical examination of the contained alkaloids would prove of particular interest.

The procedure for the separation of the alkaloids first recorded in the case of *Adlumia fungosa* (3) was again adopted. No difficulty was experienced in isolating *protopine* and *cryptopine* in a state of purity. The same fraction also contained a small amount of *α-allo-cryptopine*, and this is the first recorded case in which these three alkaloids have been found in a single species, although another case, as yet unpublished, is that of *Dicentra cucullaria*. Exhaustive examination of the mother liquors failed to reveal the presence of the as yet synthetic *cryptopalmatine*, but two further alkaloids were isolated in small amounts. One of these proved to be identical with *capnoidine*,  $C_{16}H_{15}O_6N$ , first isolated from *C. sempervirens* (4). The second, alkaloid-*η*, melting at 180° C.\*, is almost certainly represented by  $C_{21}H_{21}O_6N$ , two methoxyls being present, but in spite of these facts it is not identical with *adlumine*. Its further examination is reserved for the time being, particularly since it has been found in much larger quantity in *C. ophiocarpa*.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

<sup>2</sup> Chemist, National Research Laboratories, Ottawa.

\* All melting points are corrected.

Corlumine,  $C_{21}H_{21}O_6N$ , and corlumidine,  $C_{20}H_{19}O_6N$ , which were isolated have been previously described (6), and these together with bicuculline, all of which are phthalide isoquinoline alkaloids, constitute a substantial fraction of the total bases. A small amount of a new phenolic base, alkaloid- $\theta$ ,  $C_{16}H_{17}O_3N$ , m.p.  $183^\circ C.$ , is of interest in that it appears to be a lower homologue of a new alkaloid recently isolated from *C. aurea*. Finally, mention may be made of the presence of an alkaloid first isolated by Knörck (2) from *C. cava*. Its constitution was elucidated by Gadamer, Späth and Mosettig (1) as 2 : 9-dihydroxy-3 : 10-dimethoxy-tetrahydro-protoberberine. In view of the fact that it has not previously been named and in view of its moderate abundance in the plant under discussion the name, *Scoulerine*, is now proposed for it. The interesting fact emerges that scoulerine is the only representative of the large group of known tetrahydro-protoberberine alkaloids in this plant in spite of the readiness with which phytochemical methylation and methylenation are affected. In this connection it is pertinent to note that alkaloid- $\epsilon$  isolated from *Dicentra oregana* (5) proved on further examination to be identical with *l*-corypalmine, methylation with diazomethane yielding *l*-tetrahydro-palmatine. In the latter plant therefore corypalmine is the only representative of the protoberberine type.

### Experimental

The procedure described in detail in a previous communication (3) was used without modification. The following is a summary, the designations having the significance previously used.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—Bicuculline in part.

EC—Phenolic bases extracted from alkaline solution, by means of ether,—Alkaloid- $\theta$ .

BCE—Phenolic and lactonic bases precipitated by carbon dioxide,—Bicuculline, Corlumine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—Protopine, Cryptopine,  $\alpha$ -Allo-cryptopine, Capnoidine, Alkaloid- $\eta$ .

ES—Phenolic bases extracted from alkaline solution by means of ether—?

BSE—Phenolic bases precipitated by carbon dioxide,—Corlumidine, Scoulerine.

There was available 10.6 kg. of dried plant material, roots included, which had been collected during its flowering period.

### Isolation of Bicuculline

Owing to the fact that bicuculline is only slowly dissolved by aqueous alkali, a considerable portion of it appears in the non-phenolic fraction and is conveniently crystallized from this. The remainder was taken through alkali and reprecipitated by means of carbon dioxide. This constitutes the crude amino-acidic alkaloid previously recognized as bicucaine. It has not been found convenient to recrystallize this directly. It was dissolved in dilute

hydrochloric acid, the solution heated on a steam bath for several hours, cooled, and cautiously basified with ammonia. The precipitated granular base was then dried and crystallized by adding methanol to a concentrated chloroform solution. The recrystallized base either alone or admixed with authentic bicuculline melted at  $177^{\circ}\text{C}$ ., then slowly solidified and on further heating melted again at  $194\text{--}195^{\circ}\text{C}$ . The mother liquors were combined and the residual chloroform removed by repeated evaporation with methanol. In the course of several days a further small amount of bicuculline crystallized. The final mother liquor was neutralized with methanolic hydrogen chloride and cautiously treated with ethyl acetate until the incipient turbidity just disappeared on mixing. During the course of several weeks a small amount of bicuculline hydrochloride crystallized out. It was removed by filtration and cautious washing with ethyl acetate-methanol. The total yield of bicuculline was 20.6 gm. (0.20%).

#### *Isolation of Corlumine*

The final filtrate from the bicuculline hydrochloride was diluted with water and the organic solvents boiled off. The filtered solution was basified with excess potassium hydroxide and a slight turbidity removed by filtration. The clear filtrate was then cautiously treated with an excess of a saturated solution of ammonium chloride. The precipitated base which crystallized at once in slender needles was filtered off, washed, and dried. As thus obtained, the lactonic ring is opened and recrystallization from methanol could not be carried out without a nucleus. The latter was obtained in the following manner, which must however be regarded as fortuitous. A portion of the above amino-acidic alkaloid was dissolved in hot dilute hydrochloric acid and the cooled solution basified with excess ammonia. Ether extraction followed by chloroform extraction yielded two separate fractions. Even in the amorphous condition corlumine however is only sparingly soluble in ether. The residues remaining after the removal of the respective solvents were treated with sufficient methanol to yield a thin syrup. The solvent slowly evaporated at room temperature and brittle pale yellow residues remained. These residues were again treated with methanol and heated on a steam bath, during which process crystallization of the fraction from the chloroform extract ensued with some vigor. Nucleation of the ether extract fraction also induced immediate crystallization. Furthermore, nucleation of a hot methanolic solution of the above-mentioned precipitated base also induced crystallization. As thus obtained *corlumine* melted at  $158^{\circ}\text{C}$ . Repeated recrystallization from hot methanol in which the alkaloid is appreciably soluble raised the melting point to  $159^{\circ}\text{C}$ .  $[\alpha]_D^{25} = +77^{\circ}[\text{c} = 0.8 \text{ in chloroform}]$ . It may be added that the influence of the solvent is such that by a unique coincidence the optical activity in dry methanol is zero. The addition of hydrochloric acid makes this solution strongly laevorotatory. Calcd. for  $\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}$ ; C, 65.80; H, 5.48; N, 3.66; 2 OMe, 16.15%. Found: C, 65.51; H, 5.50; N, 4.08; OMe, 15.85%.\*

The yield of purified alkaloid was 13.5 gm. (0.12%).

\* All analytical figures are the mean of duplicate analyses.



#### *Isolation of Alkaloid-θ*

The fraction EC contained only a small amount of alkaloid some of which consisted of the non-phenolic protopine and cryptopine. The fraction soluble in aqueous potassium hydroxide was removed in this medium and the filtered solution treated with ammonium chloride. The precipitated base was filtered off, washed with water, dried and recrystallized twice from methanol in which it is moderately soluble. Large colorless flat plates melting at 183° C. were thus obtained. Yield, 0.2 gm. Calcd. for  $C_{16}H_{17}O_3N$ ; C, 70.85; H, 6.27; N, 5.17; 1 OMe, 11.98%. Found: C, 70.24; H, 5.97; N, 4.99; OMe, 9.61%.

Owing to the paucity of this alkaloid, adequate characterization was not possible. A small amount was methylated with diazomethane in methanol and yielded a non-phenolic base melting at 162° C. This does not appear to be identical with any known substance.

#### *Isolation of Protopine*

When this alkaloid is present in large amount or if crystals of the stable form (m.p. 211° C.) are available, its crystallization from suitable solvents is a very facile process. In the present case the fraction BS after thorough washing and drying was dissolved in chloroform and the filtered solution evaporated to a thin syrup. The addition of hot methanol and a nucleus immediately yielded a copious crop of slightly impure protopine. The mother liquor was freed largely of organic solvent and the residue dissolved in hot methanol. The filtered (charcoal) solution yielded on seeding with protopine another small crop of this alkaloid. The total yield was 15.5 gm. (0.15%) The protopine as thus obtained was dissolved in dilute hydrochloric acid and the hot filtered solution (charcoal) basified with potassium hydroxide. The dried base obtained in the usual manner was recrystallized from chloroform-methanol. This product consisted for the greater part of the multifaced crystals of protopine which melted at 211° C. either alone or in admixture with an authentic specimen. There was present, however, a number of large deep rectangular plates slightly yellowish in color and melting at 235° C. These were removed mechanically for the greater part. In a rapid recrystallization of the protopine the above base remained in solution. The filtrate (methanolic) was acidified with concentrated hydrobromic acid and the sparingly soluble protopine hydrobromide filtered off. The filtrate from this was diluted with water, the organic solvents boiled off, and the solution basified. The precipitated base was recrystallized from chloroform-methanol and it melted at 235° C. (*vide infra*).

#### *Isolation of Cryptopine*

The mother liquor from which the protopine had crystallized was boiled with charcoal and the filtered solution evaporated to a thin syrup. In the course of several days a crop of crystals had separated. When this was repeatedly extracted with hot methanol only a small amount of protopine remained undissolved. The combined extract was evaporated to a small volume during which process a little more protopine separated. The filtrate



from this on further evaporation deposited colorless crystals which when recrystallized from methanol (m.p. 219–220° C.) and again from chloroform-methanol melted at 221° C. Admixture with authentic cryptopine did not depress this melting point. The color reactions were those of cryptopine. The total amount obtained from this plant was 0.4 gm. (0.004%).

#### *Isolation of Capnoidine*

The small quantity of alkaloid (melting at 235° C.) isolated incidentally during the purification of the protopine proved to be capnoidine. The remainder was obtained from the mother liquors which had yielded the cryptopine. This was evaporated somewhat and acidified with hydrobromic acid. A small amount of protopine hydrobromide separated. The filtrate was freed of organic solvent and the base regenerated from its clarified aqueous solution by means of potassium hydroxide. The recovered base was dissolved in chloroform and the filtered solution evaporated to a small volume. The addition of methanol induced immediate crystallization of a base which melted indefinitely at 232° to 236° C. When this was recrystallized twice more from chloroform-methanol it consisted of brilliant colorless stout prisms melting at 238° C. The fraction from the protopine also melted at 238° C. and when admixed with a specimen of capnoidine (4) melting at 236° C. the mixture melted at 236–237° C. The total yield was 0.2 gm. Calcd. for  $C_{19}H_{16}O_6N$ ; C, 64.59; H, 4.25; N, 3.97%. Found: C, 65.32; H, 4.73; N, 4.08%; OMe—negative.

Owing to a suspected relation of this alkaloid to bicuculline, the above formula is preferred to one having two more hydrogen atoms.

#### *Isolation of Alkaloid- $\eta$*

The filtrate from the capnoidine was repeatedly evaporated with methanol to remove the chloroform, and set aside as a thin syrup. In the course of several days a small quantity of ill-defined crystals had separated. This proved to consist partly of protopine but the greater fraction of it proved to be appreciably soluble in hot methanol. Evaporation of this solution to a small volume and inoculation with a crystal reserved for the purpose rapidly yielded a crop of large colorless plates melting sharply at 180° C. It did not give the protopine color reactions and recrystallization did not raise the melting point. The yield was about 0.2 gm. Calcd. for  $C_{21}H_{21}O_6N$ ; C, 65.80; H, 5.48; N, 3.66; 2 OMe, 16.15%. Found: C, 65.77; H, 5.41; N, 4.02; OMe, 15.92%.

#### *Isolation of $\alpha$ -Allo-cryptopine*

The isolation of the above-mentioned alkaloids, four in number, from the fraction BS was a comparatively tedious process, and in many instances repetition of the procedure was necessary to eliminate or isolate fairly completely any particular constituent. There was ultimately obtained a final residue from which none of the known constituents could be isolated. This was purified via dilute hydrochloric acid, basification, and ether extraction, and then consisted of an almost colorless resin. On the supposition that the

above-mentioned alkaloid might be present, and in view of its strong color reaction with sulphuric acid, a crystal of  $\alpha$ -allo-cryptopine was added to its methanolic solution. Crystallization was immediate and the separated alkaloid melted at 159–160° C. either alone or in admixture with an authentic specimen of  $\alpha$ -allo-cryptopine. The quantity obtained was 0.1 gm.

There remained finally about 0.1 gm. of residue from this fraction. This was exhaustively examined in the hope that the hitherto exclusively synthetic cryptopalmatine might be found. Such an eventuality seemed particularly likely in view of the co-occurrence of the other three possible variants. By means of a procedure too elaborate to detail, however, only some of the above-described alkaloids could be isolated, so that eventually only a minute amount of uncrystallized residue remained.

#### *Isolation of Scoulerine*

Owing to the virtual insolubility of scoulerine hydrochloride in cold water, the greater portion of this alkaloid was obtained as the hydrochloride when the total base mixture in the chloroform extract AC was treated with dilute hydrochloric acid. The solid was collected on a filter, washed, and recrystallized from hot water in which it is appreciably soluble. The remainder of the scoulerine was found in the fractions BSE and EES. In both cases the dried fractions in methanol were acidified with concentrated hydrochloric acid. The sparingly soluble hydrochlorides which separated were recrystallized from hot water and in both cases melted with effervescence at 286° C. when rapidly heated. With cold concentrated sulphuric acid it yielded a strong greenish blue solution which did not change on standing overnight. Heating changed this to a deep purple which remained stable.

The free base was regenerated by cautiously adding ammonia to a rapidly cooled aqueous solution of the hydrochloride. The precipitated base readily became crystalline. It was recrystallized twice from hot methanol in which it is readily soluble,—grayish fine needles. When slowly heated it began to sinter at 192–196° C. but when placed in the bath at 190° C. it melted at 204° C. with but little immediate decomposition.

Gadamer and co-workers record the melting point as 192–193° C. (? corr.). The yield of purified alkaloid from all fractions was 6.1 gm. (0.06%). Calcd. for  $C_{19}H_{21}O_4N$ ; C, 69.74; H, 6.40; N, 4.28; 2 OMe, 18.96%. Found: C, 69.39; H, 6.45; N, 4.96; OMe, 19.47%.

The identity of this alkaloid with that of Knörck (2) is difficult to prove beyond question in the absence of an authentic specimen for comparison. The respective properties are however in complete accord. Furthermore, methylation with diazomethane yielded the known *l*-tetrahydropalmatine, identical in all respects with an authentic specimen from *C. aurea*.

#### *Isolation of Corlumidine*

The mother liquors from which the scoulerine hydrochloride had been crystallized were combined, diluted with water and the methanol expelled on a steam bath. The filtered aqueous solution was basified with ammonia

and the collected base dissolved in chloroform. The filtered solution was evaporated on a steam bath and the residue repeatedly evaporated with methanol. Crystallization of a sparingly soluble base shortly took place. After filtering, washing with methanol, and drying, *corlumidine* as thus obtained melted at 236° C. It consisted of stout colorless prisms, the melting point of which could not be appreciably raised by recrystallization. The total yield was 2.3 gm. (0.02%).  $[\alpha]_D^{25} = +80^\circ [c = 0.4 \text{ in chloroform}]$ . Calcd. for  $C_{20}H_{19}O_6N$ ; C, 65.04; H, 5.15; N, 3.79; 1 OMe, 8.40%. Found: C, 64.84; H, 5.27; N, 4.06; OMe, 8.20%.

#### *Isolation of Fumaric Acid*

The residue from the ether extract LC was extracted with several portions of cold water and the filtered solution evaporated to a small volume. The acid which separated on cooling was recrystallized from hot water and proved to be identical with authentic fumaric acid.

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## THE ALKALOIDS OF FUMARIACEOUS PLANTS

XIII. *CORYDALIS SIBIRICA* Pers.<sup>1</sup>BY RICHARD H. F. MANSKE<sup>2</sup>

## Abstract

Ten alkaloids have been isolated from this plant, of which the following five are known:— protopine (0.47%), cryptopine (trace), bicuculline (0.10%), corlumine (trace), and scoulerine (trace). Alkaloid- $\theta$ , previously found only in *Corydalis scouleri*, was present in traces. In addition, three non-phenolic alkaloids, all of which appear to be new, have been isolated, namely: - $\kappa$ ,  $C_{19}H_{17}O_5N \cdot CH_2OH(?)$ , - $\lambda$ ,  $C_{18}H_{15}O_5N$ , and - $\mu$ ,  $C_{18}H_{17}O_5N$ , the latter two containing two methoxyl groups each. Finally a phenolic alkaloid, - $\iota$ ,  $C_{21}H_{21}O_4N$ , containing one methoxyl group, is present in minute amounts.

*Corydalis sibirica* Pers. is a native of the Himalayan regions of Asia. In appearance it does not closely resemble any American species. It is a tall, erect, somewhat branched biennial or facultative annual with long yellow tap roots which emit a pronounced nitrous odor when freshly pulled from the ground. The corolla is yellow, the upper spurred petal being marked with several longitudinal brown stripes and tipped with green. The seed pod is flat and curved and at maturity discharges the jet black seeds with considerable force when disturbed. The appearance of the flower as well as that of the seed pods is very similar to that of an eastern Asiatic species, namely, *C. ochotensis*, now under investigation. In all other respects the two plants are easily distinguishable. The stem is glaucous green and prominently striated with red. The compound finely dissected leaves are bright green above and pale beneath, the margins and particularly the tips of the ultimate segments being marked with red.

The material for the present investigation was grown in a local garden and in part at the Central Experimental Farm, Ottawa. The author is greatly indebted to Mr. John Adams who, in this as well as on numerous other occasions, has provided facilities for propagating plants for experimental purposes. The author is further indebted to Dr. Arthur W. Hill, Director of the Royal Botanic Gardens, Kew, who kindly authenticated the species under consideration.

Our chemical knowledge of Asiatic *Corydalis* spp. is considerably limited and except for *C. ambigua* (1, 2, 3) those species which have been investigated at all have been investigated only cursorily. It seemed therefore highly desirable to investigate a number of these species, particularly in view of the fact that hitherto very rare alkaloids may be found in somewhat larger quantities. To a certain extent this has already been realized, and it is confidently expected that further investigations will yield some of the rarer alkaloids in sufficient quantity for their chemical examination.

<sup>1</sup> Manuscript received September 22, 1936.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

<sup>2</sup> Chemist, National Research Laboratories, Ottawa.

Although the examination of this species is not quite complete, it seems desirable to place on record the results obtained to date. It is proposed to continue the investigation when more material becomes available. For the work here recorded there was available a total of 7.6 kilos of dried material.

The protopine fraction proved to be quite complex and has yielded thus far only protopine, cryptopine, and a third as yet unidentified alkaloid. This, alkaloid- $\kappa$ , retains solvent of crystallization most tenaciously, melts with some effervescence at 139°, and yields analytical figures which indicate  $C_{19}H_{17}O_5N \cdot CH_3OH$ . Thus far no derivative suitable for the analysis has been obtained. Two other alkaloids, - $\lambda$ , and - $\mu$ , in the non-phenolic bicuculline fraction may be related to the above. They melt at 212° and 236° C. and yield analytical figures in substantial agreement with  $C_{19}H_{19}O_5N$  and  $C_{18}H_{17}O_5N$  respectively, two methoxyl groups being present in each alkaloid. In this connection it may be permissible to anticipate a communication dealing with *Dicentra chrysantha*, during the examination of which an alkaloid,  $C_{18}H_{15}O_5N$ , presumably related to these bases, has been isolated. An alkaloid,  $C_{21}H_{23}O_5N$ , isolated from *C. cava* by Knörck (4), also appears to belong to this group.

Bicuculline was readily isolated and the mother liquor from this yielded the recently described corlumine (6, 7). In addition to the above-mentioned seven non-phenolic bases, three phenolic alkaloids were obtained. One of these proved to be identical with scoulerine recently isolated in quantity from *C. scouleri* (7). A small amount of alkaloid- $\theta$ , also first found in *C. scouleri* (7), was present. Finally, an alkaloid (- $\iota$ ),  $C_{21}H_{21}O_4N$ , containing one methoxyl and melting at 248° C., was obtained.

### Experimental

The alkaloids were isolated by the procedure first detailed in the case of *Adlumia fungosa* (5), and the designations of the various fractions there recorded are used here with the same significance. The following is a summary of the subsequent experimental part. It may be noted that the careful execution of this scheme not only facilitates the isolation of the individual alkaloids, but their identity when they are already known is determined to a considerable extent by the fraction in which they are found.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases—Bicuculline in part, Alkaloid - $\lambda$ , Alkaloid - $\mu$ .

EC—Phenolic bases extracted from alkaline solution by means of ether,—Alkaloid - $\theta$ , Alkaloid - $\iota$ .

BCE—Phenolic and lactonic bases precipitated by carbon dioxide,—Bicuculline, Corlumine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—Protopine, Cryptopine, Alkaloid - $\kappa$ .

ES—Phenolic bases extracted from alkaline solution by means of ether—?

BSE—Phenolic bases precipitated by carbon dioxide,—Scoulerine.

\* All melting points are corrected.

### *Isolation of Bicuculline*

The isolation and identification of this alkaloid have been repeatedly described. The most detailed account is given in a communication dealing with *C. scouleri* (7). The application of that procedure to fractions (BC) and (BCE) readily yielded pure bicuculline to the extent of 0.10%. It was identified by mixed melting point determination as well as by its general appearance and behavior.

### *Isolation of Corlumine*

The removal of the bicuculline was largely accomplished by direct crystallization from methanol, the remainder being obtained as hydrochloride from methanol-ethyl acetate. Removal of the solvents from the filtrate yielded a pale brown viscous residue which was dissolved in water, and the filtered solution was basified with excess potassium hydroxide. The turbid solution was filtered and treated with excess ammonium chloride. The precipitated carboxylic base was filtered, washed, dried, and dissolved in hot methanol. Evaporation of the filtered solution to a small volume and nucleation with a crystal of corlumine immediately yielded a crop of colorless to pale yellow stout needles. As thus obtained, the alkaloid melted at 158° C., and when recrystallized from methanol with the aid of charcoal it melted sharply at 159° C. and this melting point was not depressed when the alkaloid was admixed with a specimen of corlumine from *C. scouleri*.

### *Isolation of Alkaloid- $\epsilon$*

As the ether extract representing fraction EC was evaporated, a sparingly soluble alkaloid readily separated in almost colorless slender needles. This was filtered off, washed with ether and with methanol, and dissolved in a large volume of boiling chloroform in which it is only sparingly soluble. The filtered solution was rapidly evaporated to a small volume and hot methanol added. Crystallization of colorless to pale pink fine prisms was almost instantaneous. The filtered, washed and dried alkaloid melted at 248° C. with but little previous sintering or decomposition. Calcd. for  $C_{21}H_{21}O_4N$ ; C, 71.89; H, 5.98; N, 3.99; 1 OMe, 8.83%. Found: C, 71.24; H, 5.97; N, 3.99; OMe, 8.73%\*.

### *Isolation of Alkaloid- $\theta$*

The ether and methanolic filtrates from which alkaloid- $\epsilon$  had been crystallized were evaporated to a small volume, neutralized with concentrated hydrochloric acid and treated with enough methanol to yield a thin syrup. In the course of several days a sparingly soluble hydrochloride had separated. This was dissolved in water and the base regenerated by the addition of ammonia. The crystalline precipitate was recrystallized twice from methanol, and it then melted at 183–184° C. In admixture with a specimen of alkaloid- $\theta$  from *C. scouleri* there was no depression in melting point, although in either case the melting point was not very sharp, some darkening and sintering taking

\* All analyses are the means of duplicates.



place several degrees lower. There is still some ambiguity in regard to the empirical formula of this alkaloid. The expression  $C_{17}H_{19}O_4N$  is probably as satisfactory as  $C_{16}H_{17}O_3N$  previously suggested (7). It is expected that methylation and analysis of the methyl ether will serve to dispose of this uncertainty.

#### *Isolation of Alkaloids- $\lambda$ and - $\mu$*

The mother liquor of fraction BC, from which most of the bicuculline had been separated by crystallization, was heated for a short time with methanolic potassium hydroxide in order to remove any remaining lactonic alkaloids. Water was added and the insoluble resinous base dissolved in aqueous oxalic acid. A turbidity was removed by filtration and the regenerated and dried base dissolved in hot methanol. A small amount of ill-defined fine needles separated in the course of several days. This proved to be a mixture and was largely separated into two constituents by extraction with hot methanol. The extract, on evaporation to a small volume, yielded large well developed prisms which melted at  $212^\circ\text{C}$ . Recrystallization failed to raise this melting point. In contact with concentrated sulphuric acid, it yielded a brown solution which shortly became pink, and, on heating, changed first to yellow and then to brown. This alkaloid is provisionally referred to by the Greek letter  $\lambda$ . Calcd. for  $C_{19}H_{19}O_5N$ : C, 66.87; H, 5.57; N, 4.11; 2 OMe, 18.18%. Found: C, 66.92; H, 5.69; N, 4.11; OMe, 16.24%.

The fraction above referred to, which remained insoluble in hot methanol, was dissolved in hot chloroform in which it is only moderately soluble. The filtered solution was evaporated to a small volume and treated with hot methanol. The base, which rapidly crystallized, was recrystallized by the same procedure and then melted at  $236^\circ\text{C}$ . This is alkaloid- $\mu$ . Calcd. for  $C_{18}H_{17}O_5N$ : C, 66.06; H, 5.20; N, 4.28; 2 OMe, 18.96%. Found: C, 66.01; H, 5.47; N, 4.34; OMe, 16.05%.

The filtrate from which the mixture of these two bases had crystallized was neutralized with hydrochloric acid and repeatedly evaporated with ethyl acetate. A small amount of a hydrochloride, sintering at  $238^\circ\text{--}242^\circ\text{C}$ . and melting with effervescence at  $247^\circ\text{C}$ ., separated in the course of several days. This salt is only sparingly soluble in methanol or water and proved to be the hydrochloride of alkaloid- $\kappa$  (*vide infra*). The mother liquor from this hydrochloride was diluted with water, the organic solvents boiled off, and the filtered solution basified with potassium hydroxide. The ethereal solution of the liberated base was evaporated and the residue dissolved in methanol. The crystalline base thus obtained was recrystallized from chloroform-methanol, and it then melted either alone or in admixture with alkaloid- $\lambda$  at  $212^\circ\text{C}$ .

#### *Isolation of Protopine and Cryptopine*

In some preliminary work the roots of the plant under investigation were examined separately and yielded an unusually large amount of protopine, namely, 0.80%. Some of this crystallized directly as the sparingly soluble

nitrate when the aqueous solution S was being extracted with chloroform. The protopine content of the stems and leaves was 0.47%. In both cases the alkaloid was readily obtained pure (m.p. 211° C.) by direct crystallization and recrystallization with chloroform-methanol from fraction BS.

The final mother liquor, from which no more protopine could be separated by direct crystallization was neutralized with hydrochloric acid in methanol. A small amount of protopine hydrochloride separated. The filtrate from this was diluted with water and the methanol boiled off. The filtered aqueous solution was basified with potassium hydroxide and extracted with ether. A considerable quantity of resinous base, not dissolved by the ether, was extracted with chloroform. The residue from the ether solution readily crystallized in contact with methanol and the recrystallized alkaloid (about 0.1 gm.) melted at 221° C., and this melting point was not depressed when it was admixed with cryptopine. The color reaction with sulphuric acid was that of cryptopine.

#### *Isolation of Alkaloid-κ*

The chloroform extract above referred to when detailing the isolation of cryptopine was freed of solvent and the residue dissolved in methanol. The filtered solution (charcoal) was evaporated to a small volume. In the course of a few days several crystal nuclei had formed, and when these were broken up with a rod rapid crystallization ensued. The methanolic mother liquor from the cryptopine, on seeding with these crystals, also yielded the same alkaloid. It is sparingly soluble in methanol but readily soluble in chloroform, and was repeatedly recrystallized from a mixture of these solvents. The melting point of this base ( $\kappa$ ) and that obtained from the fraction BC via the hydrochloride, as well as a mixture of the two, was not quite sharp at 139° C., some effervescence due to the escape of solvent of crystallization taking place. This solvent of crystallization is most tenaciously retained. Heating in a high vacuum does not serve to determine the amount present because the alkaloid is appreciably volatile. The total yield was 2.5 gm. Calcd. for  $C_{19}H_{17}O_5N \cdot CH_3OH$ : C, 64.79; H, 5.66; N, 3.77; 1 OMe, 8.36%. Found: C, 64.34; H, 5.47; N, 3.73; OMe, 7.50%.

The color reaction is that of the protopine group. A crystal dissolved in acetic acid and treated with concentrated sulphuric acid yields an immediate and intense wine red color which changes to purple on gentle warming.

#### *Isolation of Scoulerine*

The fractions BSE and EES in a preliminary experiment were examined separately, but, since the same hydrochloride was obtained from each fraction, they were combined in subsequent experiments and worked up as follows. The dried material was dissolved in methanol and the filtered solution (charcoal) neutralized with hydrochloric acid. During the evaporation of this solution, a hydrochloride crystallized out, which, when filtered off, washed with methanol, and dried, melted with previous decomposition at 268–269° C. Admixture with scoulerine hydrochloride from *C. scouleri* did not change the



melting point. The free base was regenerated by adding ammonia to a super-cooled solution of the sparingly soluble hydrochloride. The washed and dried base was recrystallized from hot methanol in which it is readily soluble. It then melted at 198° C. and, when admixed with scoulerine and placed in the bath at 180° C., the mixture melted at 202–204° C. With cold sulphuric acid, this base as well as authentic scoulerine yields a colorless solution which, on heating, first turns brown and then deep purple.

#### *Isolation of Fumaric Acid*

The ether extract LC, on appropriate treatment, readily yielded pure fumaric acid. It was identified by comparison with an authentic specimen.

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THE VISCOSITY OF CORN STARCH PASTES<sup>1</sup>BY WILFRED GALLAY<sup>2</sup> AND ADAM C. BELL<sup>3</sup>

## Abstract

Several series of modified corn starches covering a wide range of fluidities were prepared from corn starch treated with varying dilutions of hydrochloric acid at 50° C. The fluidities were measured by means of a standard fluidity funnel, and the effect of acid concentration on the speed of modification was noted. The viscosities of the pastes were measured in the MacMichael viscosimeter and the flow-pressure relations noted. It is shown that the viscosity is dependent on the rate of shear and that the experimental data are well expressed by the exponential relation  $F = KP^n$ , where  $F$  is the flow,  $P$  is the pressure,  $K$  and  $n$  are constants. For pastes of the same concentration, there is a rapid decrease in the value of  $n$  with increasing degree of modification. Transitions from one type of flow to another are shown in the same viscosity measurement at different driving pressures. Microscopic examination shows that the dispersed phase of ordinary starch pastes consists of swollen starch granules. The viscosity of a starch paste which has undergone no severe pretreatment depends on the deformability of the swollen granules and on the volume relation between dispersed phase and dispersion medium.

Modified starches have become important commercial products in recent years and have found extensive use in a wide variety of industries. Generally speaking, modification of starch denotes an increased apparent solubility in water with accompanying changes in the physico-chemical characteristics of the pastes. Modification may be effected by acid treatment at normal or elevated temperatures, by a variety of oxidizing agents such as alkaline hypochlorite, permanganates, perborates, peroxides, etc., and by other agents of lesser importance. Starches capable of dispersing in cold water are prepared by previously effecting rupture or disintegration of the granules, by mechanical treatment or proper heat treatment with or without the addition of chemical agents. The present work deals with starches modified by dilute acid at temperatures below the gelatinization point, and without alteration of the granule.

Aside from a purely chemical analysis for such constituents as water, ash, protein and fat, the chief characteristic of a starch, as in the case of many other lyophilic colloids, is the viscosity in solution. Viscosity measurements have proved to be of very definite value for industrial purposes and an approximate indication of what results may be expected in use.

A review of the publications on the viscosity of starch pastes shows that in the majority of cases the pastes are assumed to be homogeneous colloidal solutions similar to sols of other high molecular weight colloids such as rubber and gelatin. That this is definitely not the case in starch pastes, unless the paste has undergone lengthy boiling with agitation or unless the starch granules have been mechanically thoroughly broken, may be seen readily

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa.

<sup>2</sup> Chemist, National Research Laboratories, Ottawa.

<sup>3</sup> Chemist, National Research Laboratories, Ottawa.

in the microscope. This has been previously pointed out by Alsberg (1), and very well demonstrated in the recent photomicrographs obtained by Sjostrom (11). One of the writers (W. G.) has carried out a large number of observations under the microscope of the pasting of various types of starches (chiefly corn and potato) of differing degrees of modification and pasted under varying conditions. The conclusions drawn from these observations agree in the main with those of the above writers. Simple gelatinization, as in the case where a starch suspension is heated above the gelatinization range with a minimum of agitation, effects a swelling of the granules with no apparent rupture. The amount of starch actually dissolved outside of the granules is extremely small. Where the starch paste is comparatively dilute, the starch granules swell to a reasonably uniform shape, the extent of swelling varying apparently with the size of the unswollen granule. In more concentrated pastes, the actual volume available is insufficient for free swelling of the granules, and distortion and crowding of the swollen granules is evident. The ease of distortion of the swollen granules varies with different starches, showing a varying rigidity of the composition of the outer portion of the granule. This results further in a variation of the closeness of packing of the swollen granules in pastes of different starches. The extent of swelling of the apparently unaltered granules, under the same pasting conditions, decreases rapidly with increased degree of modification of the starch.

Moderate applied stress insufficient to cause rupture of the granules brings about distortion of the swollen granules, with slower return to approximately the original shape on removal of the stress. It was noted qualitatively that the resistance to deformation varies with the type of starch and the extent of modification.

A starch paste may be regarded therefore as a heterogeneous system resembling in many respects an emulsion and possessing a coarsely dispersed phase of deformable swollen starch granules. The viscosity of such a system should be due chiefly to the interaction of the dispersed particles, and should be only slightly greater than the viscosity of the medium in dilute systems, rising steeply at concentrations where the volume is insufficient for freedom of flow in the system. This is true of starch pastes, the viscosity increasing at first slowly and virtually linearly with increasing concentration. With further increase in concentration, the viscosity rises enormously until a stiff gel is obtained. If such a gel is subjected to mechanical treatment sufficient to cause rupture of the crowded granules, a viscous solution is obtained which does not gel. This is due to a change in the volume relation between dispersed phase and medium, and will be further discussed elsewhere (5).

Liquids, true solutions and lyophobic sols, in accordance with the Newtonian law of flow, show a strict proportionality between the amount of flow of a liquid and the force necessary to produce the flow, up to a maximum rate of flow characterized by the onset of turbulence. In other terms, the viscosities of these systems are independent of the rate of shear employed. It has been amply shown, however, that solutions of lyophilic colloids and certain hetero-

geneous mixtures exhibit anomalous flow in that, at higher concentrations, the viscosity decreases with increasing pressure. When flow is plotted against pressure for such systems, a curve is obtained which is convex to the pressure axis. In some instances, proportionality between flow and pressure is attained at higher pressures, indicating that a laminar flow has been obtained owing to an orientation of the dispersed phase. Ostwald and his collaborators (8) have generalized this relation by dividing the whole range of rates of shear into three portions, (i) structural viscosity at low rates of shear, (ii) laminar flow at intermediate rates of shear, and (iii) turbulent flow at higher rates of shear. The rates of shear required to produce these types of flow vary with the solution in question. In some instances, evidence of structure appears only at very low rate of shear and is barely detectable. In other cases, there is virtually no laminar flow, the structural region passing almost directly into a turbulent one. Since the rate of shear is a function of both pressure and the dimensions of the capillary in the case of an efflux instrument, or of pressure and the clearance between cylinders in the case of a torsional viscosimeter, the same solution may show laminar flow or turbulence depending on the speed of flow produced by a definite pressure, which depends in turn on the dimensions of the apparatus.

The minimum value at which permanent turbulence may occur in long cylinders has been derived from the equation (10)

$$\frac{vb\rho}{\mu} = 2124$$

where  $v$  = relative velocity of cylinders, *i.e.* velocity of outer cylinder in cm. per sec.

$b$  = clearance, or one-half the difference in diameter of cylinders.

$$\frac{\mu}{\rho} = \text{kinematic viscosity} = \frac{\text{viscosity in poises}}{\text{density in gm. per cc.}}$$

In the present work, turbulence was obtained at much lower figures than those calculated from the above equation, but it has been pointed out (6) that in the similar case of the critical velocity of flow through short tubes, it was found that the shorter the tube, the lower the critical velocity. In the case of the overflow viscosimeter also (8), it has been shown that in the case of short capillaries, the critical number of Reynolds is greatly reduced and that turbulence sets in at a comparatively low rate of flow. In the present work, flow-pressure curves concave to the pressure axis have been assumed to denote turbulence, no account being taken of the possibility that centrifugal and other anomalous effects play a part. The chief purpose has been rather the investigation of structure, where such anomalous effects are in all probability negligible.

No law has yet been derived which expresses the relation between viscosity and rate of shear in colloidal solutions, and hence a number of empirical formulas have been proposed by various investigators to express approximately their results. These empirical relations and proposed substitutes for Newton's

viscous resistance law for colloidal solutions have been summarized elsewhere (7). The equation of Schwedoff-Bingham may be expressed as

$$F = K(P - f)$$

where  $F$  = rate of flow

$P$  = pressure

$K$  and  $f$  are constants.

$K$  is termed the mobility of the solution and  $f$  the yield value. According to this expression, a definite pressure expressed by the yield value is necessary to produce flow. Freundlich and Nitze (4) have measured the viscosity of potato starch pastes in a torsional viscosimeter and expressed their results in terms of this law, interpreting the extrapolated intercept on the pressure axis, or yield value, as the "flow elasticity" of the paste. Within the conditions of their experiments, no opinion could be expressed as to whether the flow-stress line curved towards the origin at low speeds of rotation.

The flow of starch pastes through capillary tubes under varying pressures was studied by Farrow and Lowe (2). The flow-stress diagram was expressed in terms of the exponential relation of de Waele-Ostwald, *viz.*,

$$F = KP^n$$

where  $F$  = rate of flow

$P$  = pressure

$K$  and  $n$  are constants.

The exponent  $n$  was found to have a value independent of the dimensions of the capillary used and increasing with increasing concentration of solution. However, discrepancies are to be noted in the comparison of results obtained with different capillaries, presumably because of the different shear employed. In subsequent work, Farrow, Lowe and Neale (3) have correlated results on starch pastes in capillary and concentric cylinder viscosimeters. Tsuda (12), using a capillary viscosimeter, shows agreement with this exponential relation in starch sols. Previous investigations in this direction have not included pastes of modified starches. Rask and Alsberg (9) have noted an exponential relation also in the case of wheat starches.

#### *Fluidities of Alkaline Corn Starch Pastes*

The most widely employed means of characterizing the extent of modification of an acid-modified corn starch in commercial practice is by an arbitrary "fluidity" rating. The starch is dissolved in an alkaline solution at room temperature, and the volume of flow through a funnel of arbitrary shape and size in a definite time is noted. The procedure is such that water has a fluidity of 100, so that fluidities ranging from 0 to 100 are possible. Actually what is measured is the reciprocal of the viscosity under the varying rate of shear afforded by the instrument. The chief advantage of the method, aside from simplicity and convenience in control work, lies in the fact that the starch is dissolved without the use of heat, thereby decreasing the error in the preparation of the paste. However, no account is taken of the rate of

shear used and each funnel must be rigidly standardized against a master funnel in order to obtain results which may be comparable from one laboratory to another. Furthermore, measurements made on alkaline starch solutions are not to be interpreted directly in terms of aqueous pastes, except by experience in individual instances.

Fluidity measurements were made on several series of acid-modified corn starches prepared in the present work. Varying concentrations of hydrochloric acid were used for each series, the other conditions of preparation being maintained constant. Fig. 1 shows the increase of fluidity with time

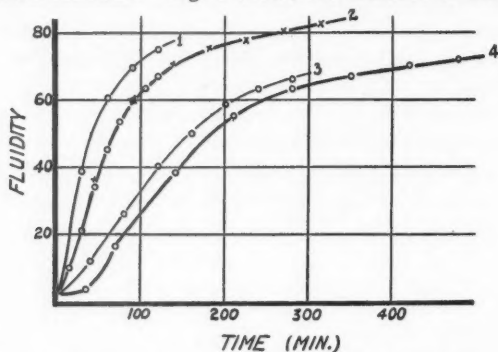


FIG. 1. Increase in fluidity of corn starch with time of modification. Concentration of hydrochloric acid by weight, based on starch—1, 2.92%; 2, 2.05%; 3, 0.97%; 4, 0.77%.

for varying concentration of acid. It is seen that the rate of modification increases with increase in acid concentration. As a measure of the rate of modification, Table I shows the time (from the graph) necessary to reach various fluidities in each series. The figures in brackets are discussed below.

TABLE I  
RATE OF MODIFICATION OF CORN STARCH AT 50° C.

Fluidity	Time (min.) for modification to the corresponding fluidity using following conc. of HCl			
	2.92%	2.05%	0.97%	0.77%
10	8 (1.00)	15 (1.88)	34 (4.25)	57 (7.13)
20	16 (1.00)	28 (1.75)	63 (3.94)	83 (5.19)
30	23 (1.00)	40 (1.74)	90 (3.91)	112 (4.87)
40	31 (1.00)	52 (1.68)	120 (3.87)	144 (4.65)
50	42 (1.00)	68 (1.62)	160 (3.81)	183 (4.36)
60	57 (1.00)	90 (1.61)	215 (3.77)	245 (4.30)
70	93	135		

The figures in brackets in Table I show the ratios of time taken to reach the corresponding fluidities based on the time for the case of 2.92% acid taken as 1. It is interesting to note that this ratio decreases with greater extent of modification, and appears to approach a value somewhat higher

than that of the inverse ratio of the amounts of acid used. It is well known that the time necessary for modification increases enormously with a comparatively small decrease in temperature, and this change of rate is very much greater than that to be expected from the temperature coefficient of a chemical reaction. The increase in rate of modification with rise in temperature near the gelatinization range is parallel with the greatly increased swelling of the granule in this range. The addition of acid apparently accelerates the changes in the starch granule accompanying modification, which probably includes an increased penetrability of the outer wall. It might be expected therefore that with smaller quantities of acid, as shown in the above table, the rate is at the start very slow, increasing with increased penetrability for the acid. A similar effect has been noted in the case of the acid modification of potato starch (5).

#### *Viscosity of Aqueous Pastes of Corn Starch*

The viscosities of these modified starches were measured at varying rates of shear with a MacMichael viscosimeter. This instrument is of the torsional type and is provided with torsion wires of varying diameters in order to permit measurements over a wide range of viscosities. It has been widely used commercially and has been fully described elsewhere (6). Although no guards are provided to reduce end effects, it has been shown (6) that these are negligible compared to the error in the set of the torsion wires, where the viscosity of the system is not too low. Above a lower limit of viscosity, liquids and true solutions show a constant ratio of deflection of the inner cylinder to the speed of rotation of the outer cylinder. Hence the instrument may be calibrated with liquids or solutions of known viscosity. Fig. 2 shows

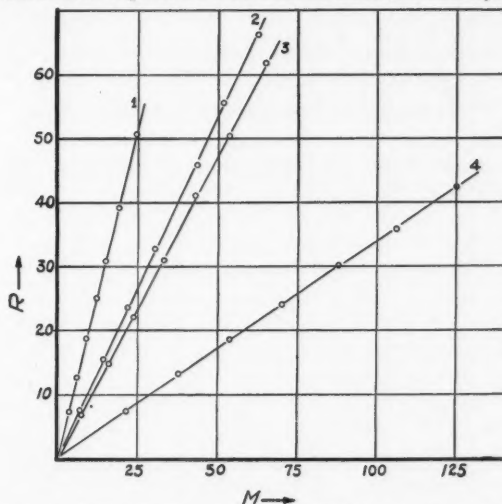


FIG. 2. Examples of laminar flow in the MacMichael viscosimeter. 1, 60% sucrose solution, wire No. 26; 2, glycerine, S.G. 1.23, wire No. 26; 3, castor oil, wire No. 22; 4, 60% sucrose solution, wire No. 30.



results obtained with several liquids and true solutions with different wires. For liquids of very low viscosity, turbulence is reached at relatively low speeds of rotation (6), but other liquids or true solutions measured up to the region of maximum safe operation of the instrument, limited by the safe limit of torsion of the wires and by the maximum speed of rotation of the outer cylinder, show strict proportionality between flow and pressure. In a number of instances, different torsion wires were used for various starch pastes in order to obtain conveniently measurable deflections. These deflections were all recalculated in terms of one torsion wire (No. 26) so that the figures are directly comparable. It was found that when the same paste was measured with two different wires and then one recalculated on the basis of the other, the agreement with the conversion factor was good, the latter being obtained directly during the calibration of the wires with standard solutions.

Figs. 3, 4 and 5 show the results obtained in determinations of the viscosities of three series of modified corn starches in the MacMichael viscosimeter. There is no indication of any yield value in the flow-stress diagrams. All the curves tend towards the origin. The transition from the structural type of flow to the turbulent type for equal concentration of starches of varying

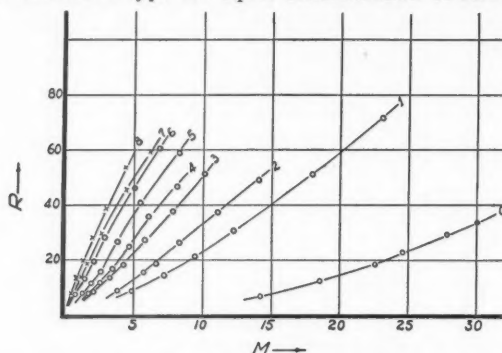


FIG. 3. Flow-pressure relations in 3% corn starch pastes, modified by 2.05% hydrochloric acid for varying periods. Curve 0; 3% paste of unmodified corn starch.

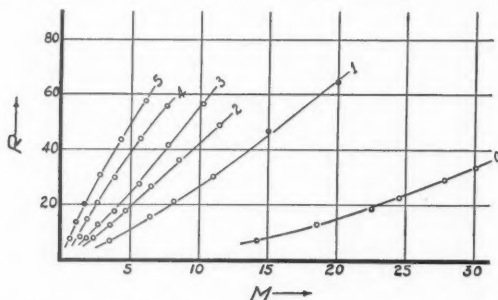


FIG. 4. Flow-pressure relations in 3% corn starch pastes, modified by 0.97% hydrochloric acid for varying periods. Curve 0; 3% paste of unmodified corn starch.

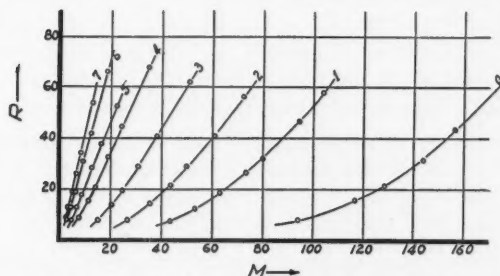


FIG. 5. Flow-pressure relations in 5% corn starch pastes, modified by 0.77% hydrochloric acid for varying periods. Curve 0; 4% paste of unmodified corn starch.

degrees of modification is seen in these curves, and appears to parallel somewhat similar experiments carried out in efflux viscosimeters. Curve 0 in each figure represents the flow-stress relation for the same concentration of unmodified corn starch, and the curves are numbered in the order of increasing extent of modification or higher fluidity. In the first series (Fig. 3), Curves 0, 1, 2 and 3 are wholly in the structural region at the rates of shear used. Curves 4 and 5 appear to show structure followed by approximately laminar flow under this range of stress. Curve 6 appears to show laminar flow succeeded by turbulent flow at greater pressure, while Curves 7 and 8 are entirely concave to the pressure axis and appear to indicate turbulence throughout\*. These transitions are clearly shown in Fig. 6 where  $M/R$ , a function of the

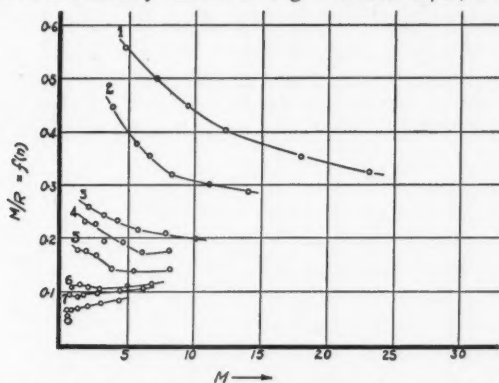


FIG. 6. Viscosities of a series of acid-modified corn starches, calculated from data represented in Fig. 3.

viscosity, has been plotted against the stress. Curve 0 is not shown in Fig. 6 for convenience of scale. In Curves 1, 2 and 3 of Fig. 6, there is seen to be a decrease in viscosity with increase in stress, Curves 4 and 5 show an initial decrease followed by approximate laminar flow, Curve 6 shows approximate laminar flow followed by slight turbulence, while in the cases of 7 and 8, very little laminar flow is noted.

\*See note on "turbulence," page 362.

Fig. 4 shows similar transitions with increasing extent of modification in the second series of starches. Curves 0, 1, 2 and 3 show structure throughout, Curve 4 a slight initial structure followed by laminar flow and then by turbulence at higher pressures, and Curve 5 turbulence virtually throughout.

The viscosities of the third series, measured at higher concentrations, are shown in Fig. 5. All of this series at this concentration show structure throughout. Curve 0 of Fig. 5 shows the corresponding results for a 4% paste of unmodified corn starch, for convenience of scale.

After a number of trials of various proposed empirical equations which have been advanced for the flow-stress relation, it was found that the simple exponential relation of de Waele-Ostwald represented the experimental results most approximately. Figs. 7, 8 and 9 show the relation between  $\log R$  and

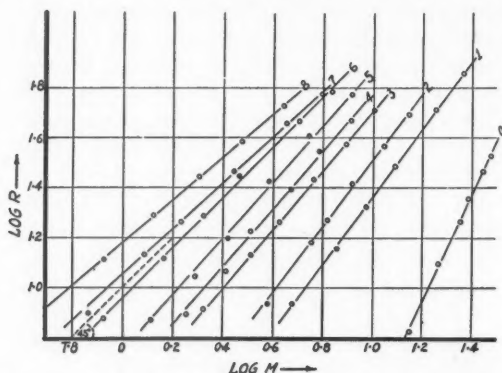


FIG. 7. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 3.

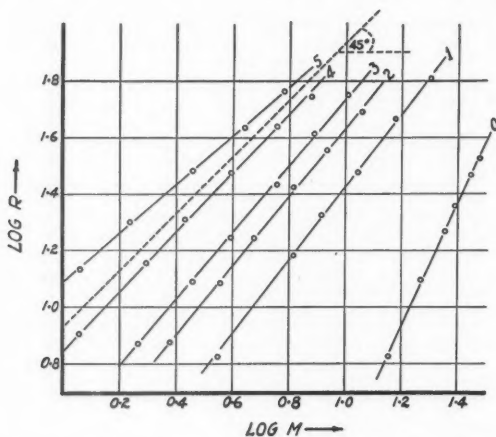


FIG. 8. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 4

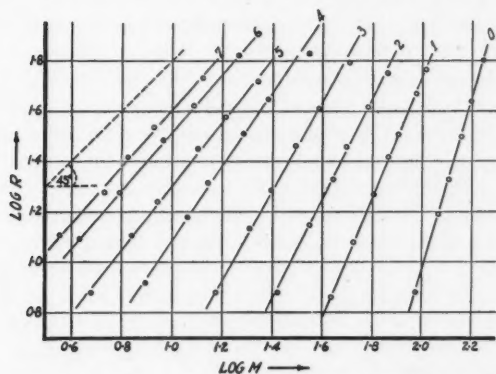


FIG. 9. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 5.

$\log M$  for the three series of acid-modified corn starches. The curves in general, with the exception of apparent deviations discussed below, show good linearity as required by the exponential relation. With increasing degree of modification in each series, there is noted a decrease in the slope of the log-log relation and hence in the value of the exponent representing the structure, together with a decrease in the constant  $K$  of the exponential equation representing a function of the coefficient of viscosity.

The possible values of the exponent  $n$  of the relation may be classified as follows:

Structural flow— $n > 1$

Laminar flow— $n = 1$

Turbulent flow— $n < 1$

As seen in the above diagrams, the relation holds well for cases where the flow is wholly of the one type within the limits of the rate of shear employed. However, in cases where transition from one type of flow to another occurs in the same paste,  $n$  is not constant and the curve cannot be satisfied by one equation. A diagrammatic representation of the fully generalized case is shown in Fig. 10, where the flow is plotted against the stress, both on a logarithmic scale. It is noted that the exponent  $n$  will, for the full generaliza-

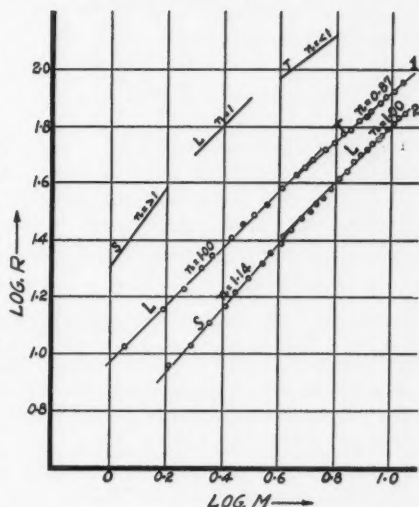


FIG. 10. Transitions among types of flow. S—structural, L—laminar, T—turbulent.

tion, have three distinct values, *viz.*, greater than 1, equal to 1 and less than 1, depending on the type of flow obtaining. In Fig. 10, there is shown also the log  $R$ -log  $M$  relation in two starch pastes which fall in the transition range. In these experiments, a large number of readings were taken in order to follow the relation more closely. Curve 1 shows laminar flow ( $n = 1$ ) for the first portion of the curve, followed by a transition to turbulent flow with  $n = 0.87$ . Curve 2 shows a structural region with  $n = 1.14$  at lower stresses followed by a transition to laminar flow at higher driving pressures. A number of similar cases have been observed, some of which show all three types of flow in the one relation. Although in Figs. 7, 8 and 9 an idealized straight line has been drawn for each relation, it is to be noted that in the cases where there is a transition from one type of flow to another at varying stresses in the same experiment, the curve may be divided into segments showing the corresponding values for  $n$ .

Tables II and III are representative of a large number of cases where structure is shown throughout the whole range, and show the order of deviation

TABLE II

VISCOSITY OF CORN STARCH, FLUIDITY 16.5  
Conc., 5% Wire No. 26  $M = 9.44R^{1.175}$

$R$ (r.p.m.)	$M$ (degrees MacMichael)	
	Obs.	Calc.
7.5	26.5	26.1
14.0	35.5	35.8
21.2	44.0	44.2
28.6	50.0	51.2
40.8	61.0	61.4
56.1	72.5	72.2

TABLE III

VISCOSITY OF CORN STARCH, FLUIDITY 34  
Conc., 3% Wire No. 30  $M = 0.359R^{1.748}$

$R$ (r.p.m.)	$M$ (degrees MacMichael)	
	Obs.	Calc.
8.2	13.0	13.1
13.5	20.0	20.0
18.3	26.0	25.9
27.0	35.5	35.8
37.5	48.0	47.5
51.0	62.0	61.6

from the exponential equation. The constants  $K$  and  $n$  were obtained graphically and the observed and calculated values of  $M$  compared.

Tables IV and V are representative of a number of cases where apparent turbulence is shown throughout. The constants  $K$  and  $n$  were obtained graphically, and the observed and calculated values of  $M$  are compared.

TABLE IV

VISCOSITY OF CORN STARCH, FLUIDITY 67  
Conc., 3% Wire No. 30  $M = 0.251R^{0.758}$

$R$ (r.p.m.)	$M$ (degrees MacMichael)	
	Obs.	Calc.
7.6	3.0	2.8
13.0	5.2	5.1
19.5	8.2	8.3
27.8	12.5	12.5
38.4	18.5	18.4
53.2	27.0	27.1

TABLE V

VISCOSITY OF CORN STARCH, FLUIDITY 58.5  
Conc., 3% Wire No. 30  $M = 0.347R^{0.787}$

$R$ (r.p.m.)	$M$ (degrees MacMichael)	
	Obs.	Calc.
13.6	7.0	7.0
20.0	10.5	10.9
30.3	17.5	17.5
43.3	26.8	26.6
57.7	37.0	36.9

Since the swelling power of the granule is decreased with increasing extent of modification, the volume occupied by a given weight of starch in a paste decreases with increasing extent of modification. For pastes of equal concentration, therefore, the interference among particles of disperse phase becomes less and the exponent  $n$ , representing a function of this characteristic, decreases with increased modification. It was found that in successive preparations of the same paste, although the conditions were held as standard as possible, the experimental deviation was of the order of 0.05 in the value of  $n$  for comparatively little structure, and about twice this amount for very concentrated pastes of low fluidity starches. Since the swollen granules vary greatly in size, varying types of packing of the granules are to be expected in different paste preparations. Slight deviations in the amount of agitation necessarily used adds also to this experimental error. Furthermore, as will be shown elsewhere (5), in the case of a concentrated paste, the comparatively slight stresses used during the actual viscosity measurement are sufficient to change the inter-particle relations with consequent change in the value of  $n$ .

The following tables show the decreasing value of  $n$ , for cases where  $n > 1$ , in the series of corn starches described above.

TABLE VI  
VALUE OF  $n$  FOR ACID-MODIFIED CORN STARCHES

No.	Fluidity	$n$
Series I, 2.05% HCl used at 50° C. Conc. of paste, 3%		
0	Unmodified	2.14
1	10	1.39
2	21	1.31
3	34	1.18
4	45	1.14
5	53.5	1.10
6	60	1.05
Series II, 0.97% HCl used at 50° C. Conc. of paste, 3%		
0	Unmodified	2.14
1	12	1.31
2	26	1.20
3	40	1.14
4	50	1.05
Series III, 0.77% HCl used at 50° C. Conc. of paste, 5%		
0	Unmodified	4.42
1	3.5	2.25
2	16.5	1.98
3	38.5	1.83
4	55.5	1.50
5	63.0	1.28
6	67.0	1.17
7	72.0	1.13

### Experimental

The starch used throughout was a high-grade commercial corn starch. Acid treatment on a large scale was carried out in an enamel-lined double-walled vessel, capacity about twenty-five gallons, fitted with suitable stirring arrangements and temperature recorder. Heating was effected by indirect steam and thermostatic control provided by an automatic valve on the entering steam line. The starch was treated in each case in 22° Bé. suspension and the temperature maintained at 50° C. Varying concentrations of acid were used in different experiments as noted above. Samples were withdrawn at definite intervals, each sample was brought to a pH of 6.3 by means

of sodium carbonate, and the suspension then filtered and thoroughly washed. Acid treatment on a smaller scale was carried out in a four-litre beaker immersed in a thermostat maintained at 50° C., the same general procedure being used.

The "fluidity" measurements were carried out in a standard fluidity funnel standardized against a master apparatus. The procedure used was as follows: 5 gm. of the starch was suspended in 10 cc. of distilled water, and 90 cc. of 1% sodium hydroxide solution added with stirring. Stirring at the rate of 180 r.p.m. was carried on for a total stirring time of three minutes after which the solution was immersed in a thermostat maintained at 25° C. After 30 min. aging, the volume of solution flowing through the fluidity funnel in 70 sec. was noted and this fluidity corrected by a calibration chart.

For viscosity measurements in the MacMichael viscosimeter, the following procedure was adopted for the preparation of all pastes. To a suspension of the starch in 5 cc. of water was added 95 cc. of boiling water from a wide-mouthed pipette, the addition being made so that the extent of agitation was approximately the same in all cases. The paste was cooled to 25° C. and placed in the viscosimeter cup, the measurement being taken immediately afterwards.

#### Acknowledgment

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## CONTRIBUTION À L'ÉTUDE D'ACER SACCHARUM

### LES AMYLASES DE LA SÈVE D'ÉRABLE ET LE POUVOIR-TAMPON<sup>1</sup>

PAR ELPHÈGE BOIS<sup>2</sup> ET ARISTIDE NADEAU<sup>3</sup>

#### Résumé

Les courbes de neutralisation obtenues avec de la sève d'érable concentrée et dialysée donnent deux paliers, qui se traduisent dans les courbes de coefficient-tampon par deux minima, au pH 4.6-4.9 et 6.5-6.7 respectivement. Ces minima correspondent aux points où la substance étudiée passe par un minimum de pouvoir-tampon analogue au point isoélectrique des protéines. Ces résultats confirment la présence de deux amylases dans la sève d'*Acer saccharum* comme nous l'avons déjà constaté (2) et que nous avons nommées sucrogène-amylase et cellobiogène-amylase.

#### Introduction

D'après Waldschmidt-Leitz (10, p. 22) les ferments sont ou simplement des substances protéiques ou des substances chimiques absorbées par une suspension colloïdale de nature protéique, jouant le rôle de protecteur. Or on sait que les protéines jouissent des propriétés des ampholytes qui se comportent à la manière d'une base libre, à pH bas, et d'un acide libre, à pH élevé. Il s'ensuit que, pour une certaine valeur intermédiaire de pH, l'ampholyte passe par un point neutre qui lui est spécifique.

Si à un tel système on ajoute une base ou un acide, il se produit au début, une faible variation de pH puisqu'une partie du réactif ajouté se combine à l'ampholyte pour former un sel jouant le rôle de tampon. Mais au point neutre les conditions sont changées; toutes les fonctions sont bloquées, il n'y a plus formation de sel. L'acide ou la base ajoutés ne servent qu'à faire varier le pH, de sorte que, le pouvoir-tampon devient faible ou nul. C'est ce que nous indiquent les courbes de neutralisation exprimant le pH d'un liquide en fonction de l'acide ou de la base ajoutés. Chaque courbe, ainsi tracée, présente une allure particulière suivant la constitution de la solution à étudier.

Si maintenant on considère, pour une même variation de pH, la quantité du réactif ajouté, on obtient une nouvelle valeur qui est le pouvoir-tampon de la solution, pour un pH donné. En d'autres termes, si on détermine la pente en chacun des points de la courbe de neutralisation on obtient une nouvelle courbe, la dérivée de la première, la courbe de coefficient-tampon, où les points neutres, spécifiques pour chaque substance, sont représentés par des minima de pouvoir-tampon analogues au point isoélectrique des protéines. Les courbes de coefficient-tampon sont beaucoup plus caractéristiques que les courbes de neutralisation.

<sup>1</sup> Manuscrit reçu le 11 juillet, 1936.

<sup>2</sup> Contribution du Laboratoire de Biochimie, Ecole Supérieure de Chimie, Université Laval, Québec.

<sup>3</sup> Professeur de biochimie à l'Université Laval.

<sup>4</sup> Etudiant gradué, Université Laval, Boursier du National Research Council of Canada.

Les premiers qui ont employé cette méthode à l'étude des solutions biologiques, semblent être Koppel et Spiro (8) dans des travaux sur l'urine des malades, Van Laer (9) dans des recherches industrielles, Hans Moser (11) qui a examiné les sérums des nourrissons rachitiques, Reiss et Vellingner (12) de Caro (4) les substances musculaires. Mais l'emploi de l'électrode à hydrogène pour la détermination du pH présentait des inconvénients à cause de sa technique assez difficile. Maintenant cette étude est facilitée de beaucoup, grâce à l'usage des électrodes à antimoine en différentiel. Cette méthode, mise au point par Vlès (16), a été employée avec succès dans différentes recherches, en particulier, les recherches sur les sérums humains par Gex (6), sur les constituants des œufs en incubation par Rubinstein (14), sur le liquide céphalo-rachidien par Bernstein (1), sur le sang de poisson par Florence et Drillhon (5), sur le lait par Bratasano (3), et sur diverses substances organiques par Roche et Reiss (13) et par Gonçalves (7). Nous avons cru bon de faire les mêmes mesures sur une solution d'amylases de sève d'érable dans le but de trouver le minimum de pouvoir-tampon qui est dans la zone du pH correspondant au maximum d'activité, et où la solubilité est la plus faible d'après les travaux de Sherman, Thomas et Caldwell (15), puisqu'il y a certainement analogie entre le point isoélectrique et le point neutre, caractérisé par le minimum de pouvoir-tampon.

### Partie expérimentale

Dans le but d'obtenir une solution de ferment débarrassé de toutes substances étrangères, la sève d'érable, recueillie dans des foles contenant du toluol, est concentrée dans le vide aussitôt que possible à une température de moins de 30° C. jusqu'à une teneur en solide de 30% environ. Puis le concentré, placé dans des sacs en cellophane, est dialysé, dans un courant d'eau distillée et refroidie, jusqu'à disparition des sucres. Cette solution, ne contenant plus que des substances à l'état colloïdal est alors prête à la détermination du pouvoir-tampon.

Le pH est mesuré électrométriquement par la méthode de Vlès (16) qui consiste à mesurer la différence de potentiel entre deux électrodes d'antimoine placées en différentiel, dont l'une est plongée dans la solution à étudier et l'autre dans une solution de référence (acide chlorhydrique,  $N/10$ ) de pH connu,  $pH_0$ . Chacune de ces solutions est reliée par un robinet, au chlorure de potassium saturé d'une pile à calomel, la mesure étant faite au potentiomètre Leeds-Northrup, type *K* et galvanomètre à cadre mobile. Le pH est calculé à l'aide de la formule suivante.

$$pH = mV \times K + pH_0$$

$mV$  est le nombre de millivolts lus;  $K$ , la constante des électrodes d'antimoine dont la valeur est trouvée par une courbe de référence établie au moyen de solutions tampons de pH déterminé à l'électrode d'hydrogène. En portant en ordonné le pH des solutions tampons et en abscisses la force électromotrice correspondante, on détermine une série de points qui constituent la courbe de référence. On introduit 25 cc. de la solution à étudier, acidulée avec de

l'acide chlorhydrique,  $N/100$ , dans l'un des vases de l'électrode d'antimoine—l'autre électrode est toujours plongée dans de l'acide chlorhydrique,  $N/10$ ,—puis on ajoute à l'aide d'une microburette des quantités progressives d'hydroxide de soude,  $N/100$ . Après chaque addition, on agite bien avant de faire la mesure de la force électromotrice. En portant le pH, trouvé à l'aide de la formule plus haut, en fonction de la quantité de base ajoutée, on trace la courbe de neutralisation à partir de laquelle on calcule la courbe de coefficient-tampon par la formule suivante.

$$t = \frac{\Delta m}{\Delta \text{pH}} = \frac{\Delta q \cdot n}{\Delta \text{pH} \cdot V}$$

$t$  = coefficient-tampon;  $m$  = équivalent en gramme de réactif ajouté par litre de la solution;  $\Delta q$  nombre de centimètres cubes du réactif ajouté de normalité  $n$  pour  $\Delta \text{pH}$  déterminé, dans  $V$  volumes en centimètres cubes de la solution à étudier. La courbe de référence est refaite avant chaque courbe de neutralisation.

#### RÉSULTATS

Nous avons tracé plusieurs courbes de neutralisation et nous donnons ici les graphiques de celles faites dans les meilleures conditions. Ces courbes, dont les deux premières ont été obtenues avec de la sève dialysée et concentrée dix fois environ et la dernière avec de la sève dialysée et concentrée cinq fois environ, présentent une allure à peu près semblable, avec des paliers plus ou moins apparents qui se produisent toujours aux mêmes pH, entre 4.5–5.0 et 6.5–7.0. Nous donnons à titre d'exemple, les valeurs trouvées pour la courbe de neutralisation No. 2 et la courbe de coefficient-tampon No. 2. (Voir tableaux I et II).

TABLEAU I  
EXEMPLE DE LA COURBE DE NEUTRALISATION NO. 2

$$\text{pH} = mV \times K + \text{pH}_0 \quad \text{pH}_0 = 1.01 \quad K = 0.01925$$

NaOH, $N/100$	$mV$	pH	NaOH, $N/100$	$mV$	pH
0.00	129.5	3.50	0.48	223	5.31
0.04	131	3.53	0.51	235	5.54
0.09	133	3.57	0.56	255	5.93
0.12	134.5	3.60	0.58	264	6.10
0.15	136	3.63	0.61	279	6.38
0.18	138	3.67	0.62	295	6.70
0.22	141.5	3.73	0.64	305	6.89
0.25	148.5	3.87	0.66	318	7.14
0.28	152.5	3.95	0.695	337	7.50
0.30	158.5	4.06	0.72	349.5	7.75
0.32	162	4.13	0.75	363	8.00
0.34	168	4.24	0.78	375.5	8.25
0.36	174	4.36	0.81	384.5	8.42
0.38	182	4.51	0.84	391.5	8.55
0.40	194	4.75	0.90	401.5	8.75
0.42	199.5	4.85	0.95	409	8.90
0.45	214.5	5.14	1.00	418	9.06

Notes: 25 cc. sève dialysée et concentrée 10 fois environ acidulée avec 0.5 cc. d'acide chlorhydrique  $N/100$ .

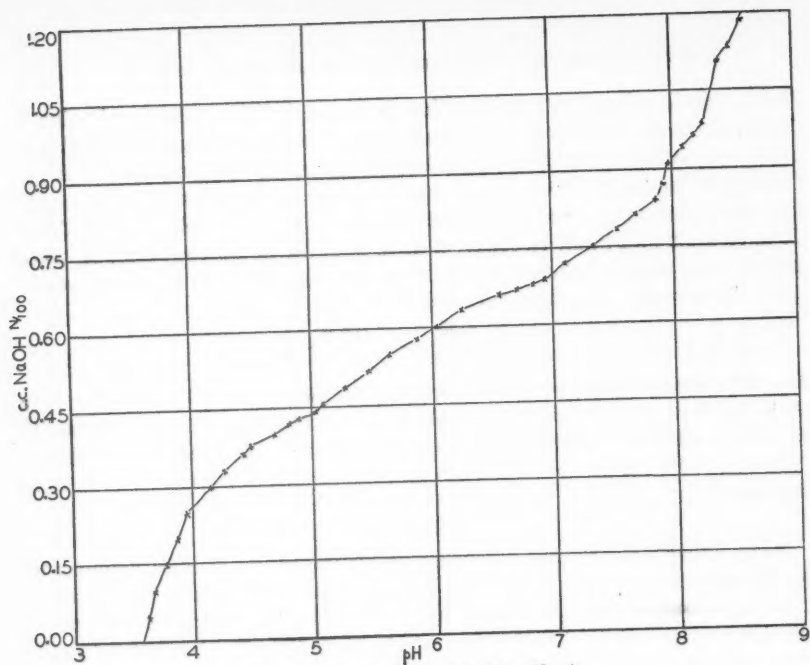


FIG. 1. Courbe de neutralisation No. 1.

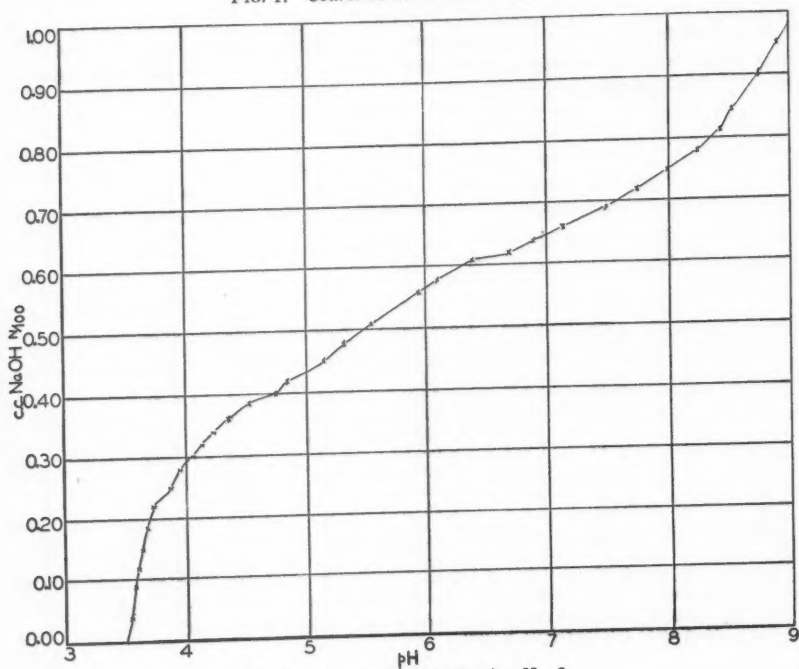


FIG. 2. Courbe de neutralisation No. 2.

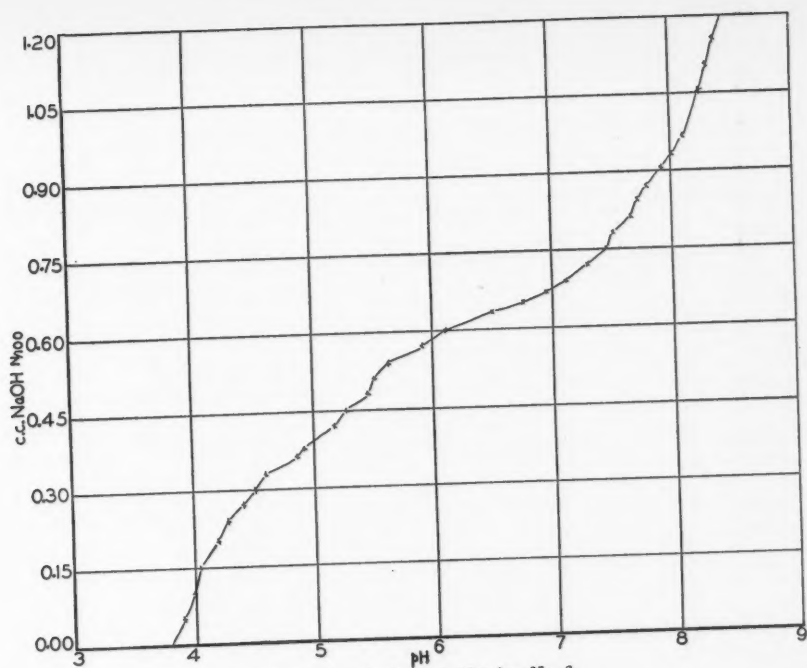


FIG. 3. Courbe de neutralisation No. 3.

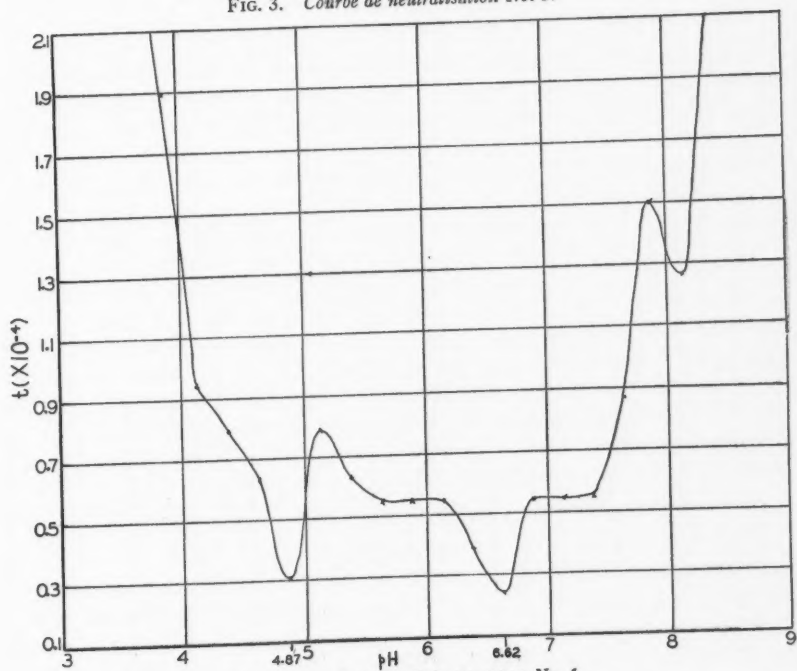


FIG. 4. Courbe de coefficient-tampon No. 1.

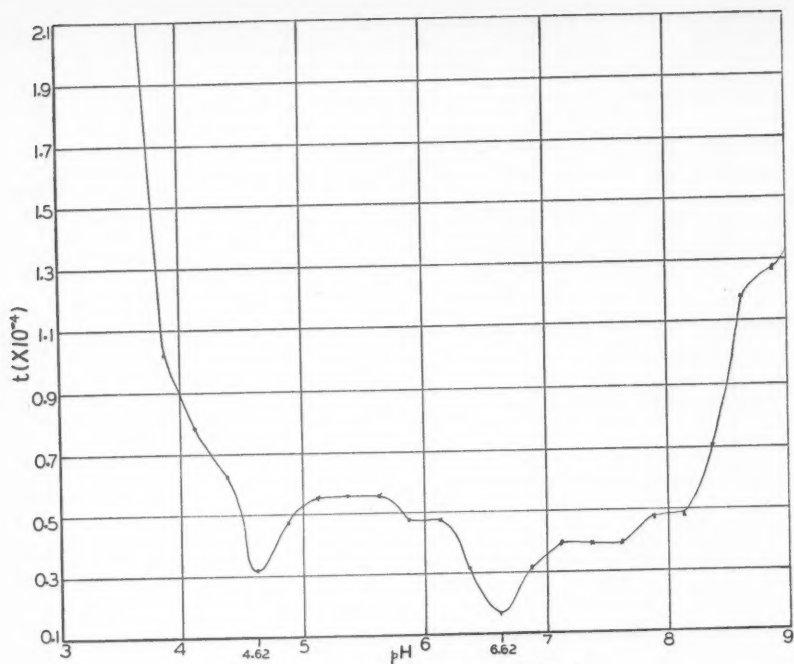


FIG. 5. Courbe de coefficient-tampon No. 2.

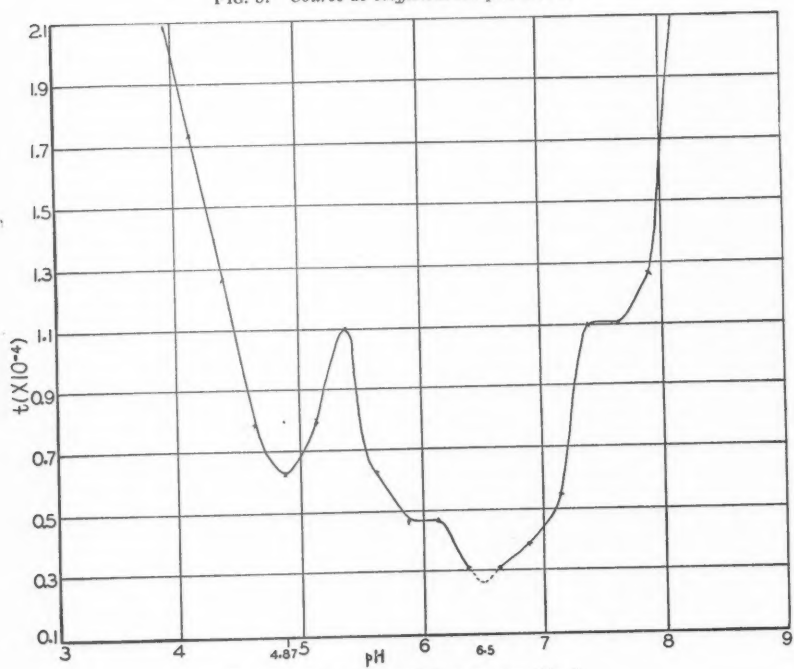


FIG. 6. Courbe de coefficient-tampon No. 3.

TABLEAU II

EXEMPLE DE LA COURBE DE COEFFICIENT-TAMPON NO. 2

$$t = \frac{\Delta m}{\Delta \text{pH}} = \frac{\Delta q \cdot n}{\Delta \text{pH} \cdot V} = \Delta q \cdot 15.70 \times 10^{-4}$$

$$n = 0.01 \quad V = 25.5 \text{ cc.} \quad \Delta \text{pH} = 0.25$$

pH	$\Delta q$ , cc.	$t(x10^{-4})$
3.62	0.225-0.00	3.53
3.87	0.29 -0.225	1.02
4.12	0.34 -0.29	0.78
4.37	0.38 -0.34	0.63
4.62	0.40 -0.38	0.31
4.87	0.43 -0.40	0.47
5.12	0.465-0.43	0.55
5.37	0.50 -0.465	0.55
5.62	0.535-0.50	0.55
5.87	0.565-0.535	0.47
6.12	0.595-0.565	0.47
6.37	0.615-0.595	0.31
6.62	0.625-0.615	0.16
6.87	0.645-0.625	0.31
7.12	0.67 -0.645	0.39
7.37	0.695-0.67	0.39
7.62	0.72 -0.695	0.39
7.87	0.75 -0.72	0.47
8.12	0.78 -0.75	0.47
8.37	0.825-0.78	0.70
8.62	0.90 -0.825	1.18
8.87	0.98 -0.90	1.26

Les paliers des courbes de neutralisation se traduisent sur les courbes de coefficient-tampon par des minima plus ou moins prononcés. Ces courbes sont beaucoup plus caractéristiques que les premières (voir les graphiques qui suivent).

Dans leur ensemble les courbes de coefficient-tampon sont comparables. Deux minima de pouvoir-tampon se produisent dans les mêmes régions de pH, séparées, dans certains cas, par un palier à peu près horizontal. La courbe No. 1 présente deux minima bien prononcés au pH 4.87 et 6.62 respectivement, avec un autre minimum beaucoup plus faible au pH 8.12 qui n'apparaît pas sur les autres courbes. Le minimum au pH 6.62 se rencontre de nouveau sur la courbe No. 2, mais il se produit un léger décalage pour l'autre minimum qui est situé au pH 4.62 au lieu de 4.87. La courbe No. 3 diffère légèrement des deux premières, mais les deux minima caractéristiques sont encore présents, l'un au pH 4.87 et l'autre au pH 6.50 (léger décalage par rapport aux courbes précédentes). Il faut remarquer, comme il a été dit plus haut, que la solution employée dans ce cas-ci provenait d'un autre échantillon de sève de concentration plus faible.

### Conclusions

De ces résultats on peut conclure à la présence de deux régions assez bien définies de minimum de pouvoir-tampon, l'une au pH 4.6-4.9, l'autre au pH 6.5-6.7, où les amylases de la sève ou mieux les substances à l'état colloïdal sont à un point neutre analogue au point isoélectrique des protéines.



Il y aurait donc dans la sève d'érable comme nous l'avons constaté antérieurement (2) deux amylases; la sucrogène-amylase et la cellobiogène-amylase hydrolysant l'amidon en sucrose et cellobiose respectivement.

La connaissance de ces points neutres peut conduire à la précipitation ou du moins, à une certaine purification de ces amylases, puisqu'elles passent alors par leur minimum de solubilité. De plus ces points de minimum de pouvoir-tampon doivent être voisins du maximum d'activité d'après Sherman, Thomas et Caldwell (15). Nous nous proposons d'étudier l'activité de ces ferments en fonction de la température et du pH, dans le but de trouver les meilleures conditions d'hydrolyse.

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